LA

# AN

## INTRODUCTION

### TO THE STUDY OF

# QUALITATIVE CHEMICAL

# ANALYSIS.

BY

LAUNCELOT WINCHESTER ANDREWS, M.A., Ph.D., ETC.,

PROFESSOR OF CHEMISTRY
AND DIRECTOR OF THE CHEMICAL LABORATORIES
AT THE STATE UNIVERSITY OF IOWA.

IOWA CITY:
A. J. HERSHIRE AND COMPANY.
1891.

# PREFACE.

The object of this work is to present to college students the main facts and methods of Qualitative Analysis with the fullness requisite for successful study, but in a form simplified by the omission of the rarer elements, and more condensed than that in which they are given in the classical *Manual* of Fresenius.

Believing that the study of this branch should always be preceded by theoretical and practical instruction in General Chemistry, an elementary acquaintance with that science is assumed. Nevertheless, all the more important qualitative reactions are elucidated by chemical equations, and but little knowledge is taken for granted, beyond that which a comprehension of the symbols and of the nomenclature implies. The nomenclature adopted is in harmony with the recommendations of the Chemical Society of London and of the Committee on Nomenclature of the American Chemical Society, except in one minor point.

It is hoped that the scheme for the systematic detection of the acid radicals, which offers some novel features, will be found elsewhere as practical and useful as an experience of some years has shown it to be at this laboratory. The aim throughout has been to discourage, so far as possible, the pernicious habit of working in a mechanical way by rule of thumb, and, for this reason, analytical tables have been excluded, with the exception of tables for the blowpipe examination of metallic and non-metallic substances, to which the suggested objection does not apply and which have been elaborated with especial care.

Numerous cross-references have made it possible to avoid many repetitions, which without them would have been necessary, and will

be, it is thought, in conjunction with copious marginal notes, a welcome feature to all those who may have occasion to use this book in the laboratory.

The author desires to express his acknowledgements to Mr. F. W. Spanutius, M. Sc., Instructor at this University, for valued assistance in the preparation of the manuscript and in testing certain methods, and to Mr. E. W. Rockwood, A. M., Demonstrator in the Medical Department, for suggestions relative to the blowpipe analysis of alloys.

al notes, a welcome
e this book in the

nents to Mr. F. W.
valued assistance in
ertain methods, and
he Medical Depart-
lysis of alloys.

# CONTENTS.

## CHAPTER I.

### METHODS AND MANIPULATIONS.

## CHAPTER II.

### REACTIONS OF THE BASES.

## CONTENTS.

## CHAPTER III.

### REACTIONS OF THE ACIDS.

1... con... com... inclu... com...

2... fied... the... lum... havi... agai... tive... the... know...

3... with... non-... ther... the... case... reac...

# CHAPTER I.

## METHODS AND MANIPULATIONS OF
## QUALITATIVE ANALYSIS.

### INTRODUCTORY.

**1.** The object of qualitative analysis is to ascertain what constituents are present in any mixture. But few of the compounds of carbon, or organic substances, are ordinarily *Object.* included, because a search for them would entail too much complication in the processes.

**2.** The means, by which inorganic substances are identified, vary according to the nature of the substance. Some of the elements will impart a characteristic color to the non-luminous flame, others may be converted into compounds *Method.* having an appearance which can be readily recognized, or again others may give rise under certain conditions to distinctive odors. Any such phenomena, which may be utilized for the identification of an element or a chemical compound, are *Reactions.* known as its *reactions*.

**3.** Very often the reactions of one substance will interfere with those of another, for example, sodium will impart to the non-luminous flame a yellow coloration, calcium an orange; therefore, neither of these substances can be recognized by the flame test when the two are mixed together. In such cases it is necessary to separate those constituents whose reactions mutually interfere.

**4.** The practice of qualitative analysis is accordingly divided into two distinct parts, namely: first, separation into groups of substances of such a character that the members of each group will not interfere with the reactions of other members of the same group: second, identification of the individual members of each group. Now, it is often impossible that the identification can be positive and conclusive, unless the separation has been complete.

*Separation of constituents.*

**5.** The student should always bear in mind that the first steps of an analysis, looking to a separation, are just as important as the last, and that success can only be attained by a conscientious attention to detail, from beginning to end. The reactions of a substance are often displayed by the addition to the body under examination of some material which may be either solid, liquid, or gaseous, and which is called a *reagent.* It is a frequent error of beginners to employ too large a quantity both of the substance under examination and of the reagent. In most cases, a drop is as good as a test tube full, and the employment of too large quantities, or too concentrated solutions, is likely to delay the work, and sometimes, to obscure the reaction.

*Reagents.*

**6.** The order in which the tests are applied for the detection of the constituents of a mixture is by no means a matter of indifference. The system, which experience has developed and which is here laid down, for the guidance of the student, is that which will most quickly lead to reliable results, and the learner should not undertake to depart from it.

*System.*

## OPERATIONS AND REACTIONS.
### FLAME TESTS.

**7.** In most chemical operations the flame of a Bunsen burner is employed as a source of heat.

This instrument is so constructed as to burn a mixture of gas and air. The flame should be of a clear, pale blue. If it emits any yellow light, the burner is out of order. A careful inspection of this flame shows that it consists of three parts.

*Bunsen flame.*

The interior portion (Fig. 1), *a*, is a cold mixture of gas

lysis is accordingly
first, separation into
that the members of
ctions of other mem-
tion of the individual
n impossible that the
e, unless the separa-

in mind that the first
on, are just as impor-
nly be attained by a
ginning to end. The
ed by the addition to
aterial which may be
ch is called a *reagent*.
ploy too large a quan-
nation and of the rea-
d as a test tube full,
ntities, or too concen-
ork, and sometimes, to

applied for the detec-
by no means a matter
perience has developed
uidance of the student,
reliable results, and the
from it.

**ACTIONS.**

he flame of a Bunsen

as to burn a mixture of
a clear, pale blue. If it
ut of order. A careful
onsists of three parts.
a cold mixture of gas
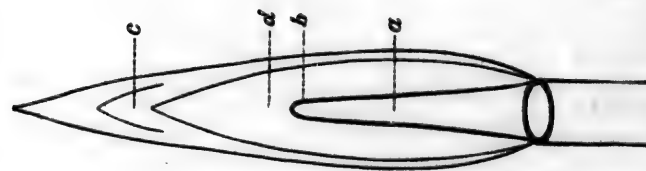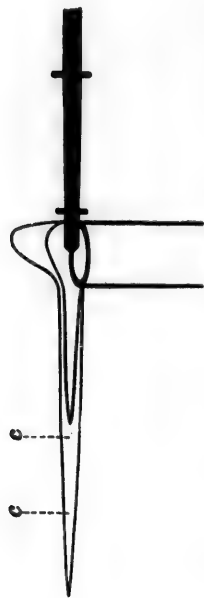
FIG. 2.
BLOWPIPE OXIDIZING FLAME.
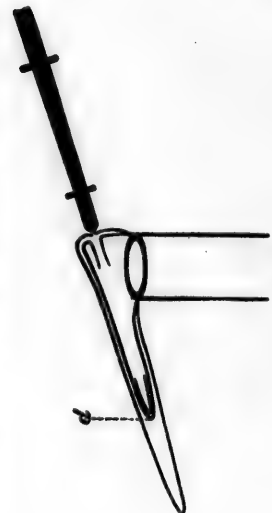
FIG. 3.
BLOWPIPE REDUCING FLAME.

FIG. I.
BUNSEN FLAME.

and air. This is immediately surrounded by a blue cone, *b*. In this layer most intense combustion is taking place. It is known as the *zone of reduction* or *deoxidizing flame*, because here the coal gas is present in excess as compared with the air. Immediately surrounding this portion of the flame is a somewhat thicker zone, which may be called the zone of fusion or outer reducing flame. Outside of this is a layer which emits so little light, that it can only be easily seen in a darkened room. *[Reducing flame.]*

This outer layer is called the mantle or the *oxidizing flame*. Here oxygen is present in excess. Many substances when held in this portion of the flame become oxidized. Take a copper wire (about No. 16) and hold it across the flame at the point *c*. Observe that it becomes coated with a black layer of copper oxide. Now depress it to a point marked *d* and observe that here the black coating of copper oxide disappears, giving place to a bright surface of metallic copper. *[Oxidizing flame.]*

By holding the wire successively in different portions of the flame, you will readily ascertain which parts are oxidizing and which are reducing in their action.

Next take a fine platinum wire and hold it across the flame in different positions. Where the wire glows most brightly the flame is the hottest. Find out in this way for yourself where the hottest portion of the flame is and always use this part of the flame when the highest attainable temperature is desired. Many substances when brought into this portion of the flame, *d*, will impart to the latter a coloration (*vide* §302). *[Zone of fusion.]*

If a platinum wire be drawn through the fingers and then held in the flame, the later will emit a yellow light, due to the sodium existing in the perspiration which adhered to the platinum wire.

The platinum wire employed for flame reactions must be scrupulously clean. It is a good plan to keep it in a test tube, immersed in hydrochloric acid and, before using it, to hold it in the flame until it ceases to color the latter. The wire should frequently be rubbed with wet sand. *[Care of Pt. wire.]*

FIG. 3.
BLOWPIPE REDUCING FLAME.

FIG. 1.
BUNSEN FLAME.

## BLOWPIPE REACTIONS.

**8.** By the use of the blowpipe, a hotter flame and, consequently, a more intense oxidizing or reducing action can be obtained than with the Bunsen flame. When the blowpipe is to be employed, turn off the air supply at the base of the burner and diminish the flame to a height of about an inch and a half.

Use of the
blowpipe.

To produce an oxidizing flame, place the blowpipe nozzle just above the tube of the burner and half way across the flame. In this position, a steady blast will give a fine pointed, blue, oxidizing flame. (Fig. 2.)

To produce a reducing flame the nozzle should be held just outside the flame and the blast should be less powerful. (Fig. 3.)

**9.** Many substances dissolve in fused borax, imparting to it a characteristic coloration. A somewhat stouter platinum wire than that which is used for flame tests (§7) forms the best support for the melted borax. For this purpose the wire is bent around the point of a pencil so as to make a closed loop, or eye, one-tenth of an inch in diameter. If the hot loop be plunged into powdered borax and then held in the blowpipe flame (at *c*, Fig. 2) the borax will fuse to a globule of colorless transparent glass, known as the *borax bead*.

Borax
bead.

To test the behavior of any body to the borax bead, it should be finely powdered and touched with the red-hot, soft bead. Some of the substance will adhere to the bead, so that when the latter is again fused, solution will take place.[1]

Soda
bead.

**10.** The *soda bead* is made and used in the same way, except that sodium carbonate takes the place of borax.

Meta-
phosphate
bead.

**11.** The *microcosmic salt bead* is made in a similar way, by fusing sodium ammonium orthophosphate, $NaNH_4HPO_4$, on the wire loop. Under the influence of a high temperature the "microcosmic salt" forms *sodium metaphosphate*,

$$NaNH_4HPO_4 = NaPO_3 + H_2O + NH_3$$

---

[1] Applications of this test are described in §§78, 106, 88. The student should practice with a bead containing a little Mn, until he can make it colorless in the reducing flame and violet in the oxidizing flame.

In the latter, almost all compounds, except silica, dissolve to a clear, sometimes colored, glass (§106).

**12.** Compounds of many metals when used in the reducing flame, on charcoal, either alone or with sodium carbonate, are reduced to the metallic state.[1]  The compound, in fine powder, is well mixed with about twice its bulk of sodium carbonate and enough water to form a stiff paste, which is placed in a slight hollow in the prepared charcoal stick,[2] and patiently fused in a strong reducing flame.

*Reduction on charcoal.*

The product is to be removed from the charcoal and rubbed with a little water to dissolve the sodium carbonate.  If any metal has been reduced, it may be found in the undissolved residue in the form of globules, spangles or powder, according to the nature of the metal, and it may be examined as to hardness, color, magnetic properties, etc.  These characteristics are often sufficient for identification.  The soft, blueish globules of lead, the brilliant white, malleable ones of silver, the yellow ones of gold, or the irregular magnetic particles of iron or magnetic spangles of nickel, may for example be certainly recognized.

**13.** Some bodies when heated alone on charcoal in the oxidizing or reducing flame produce an incrustation or *film* on the charcoal.  Such films present characteristic differences of appearance, as *color* when hot or cold, *distance* from the heated object, etc.  Some of these films are described under Tin, Lead, Bismuth, Arsenic, Mercury, etc.

*Films.*

**14.** Volatile substances when heated in a matrass, or hard glass tube, about three inches long by three-tenths of an inch in diameter, are sublimed, forming a deposit upon the cooler part of the tube; and some compounds give off a gas when heated in the same way.  Among the bodies which may be

*Matrass, or closed tube.*

[1] *Vide* §§304, 135.

[2] A piece of ordinary soft wood charcoal may be used if the prepared charcoal is not at hand.  Sometimes it is desirable to use, instead of sodium carbonate, a flux composed of three parts of sodium carbonate, two parts of potassium cyanide and one part of borax.  The materials should be fused together and powdered for use.

Matrass, or closed tube.

recognized by their behavior when heated in the matrass are to be noted the following:

| | |
|---|---|
| WATER: . . . . | Appears in drops or as a mist in the matrass. |
| AMMONIUM SALTS: | White sublimate, often odor of $NH_3$ evolved (§37). |
| ARSENIC: . . . . | Shining gray-brown or black mirror. |
| SOME SALTS AND AMAL-GAMS OF MERCURY: MERCURIC OXIDE: . | Minute globules of mercury, which when rubbed with a copper wire moistened with nitric acid, give it a silvery coating (§127). |
| MERCUROUS CHLORIDE: | Sublimes white, without fusion. |
| MERCURIC CHLORIDE: | Fuses and sublimes, yellow when hot, white when cold. |
| ANTIMONOUS OXIDE: | Fuses to a yellow liquid, sublimes as needle-shaped crystals. |
| SULPHUR AND SOME SULPHIDES: . . . | Non-crystalline sublimate, brownish yellow when hot, canary-yellow when cold. |
| ARSENIC AND ARSE-NOUS SULPHIDES: . | Sublimate dark red when hot, yellowish red when cold. |
| MERCURIC SULPHIDE: | Sublimate dull black. |
| IODINE: . . . . | Black, crystalline sublimate, violet vapours and peculiar odor. |
| SOME NITRATES AND NITRITES: . . . | Brown vapours of an acid reaction and peculiar odor (§295). |
| SOME FLUORIDES: . | Colorless gas of acid reaction, etches the glass. |
| SOME CYANIDES: . | Cyanogen gas evolved; has peculiar odor, and burns with crimson flame. |
| SOME CARBONATES: | $CO_2$ evolved; renders turbid a drop of lime water (§199). |

| SOME SULPHATES AND SULPHITES: . | $SO_2$ evolved, which has acid reaction and peculiar odor (§§194-198). |
| PEROXIDES, CHLORATES, BROMATES, IODATES, CHROMATES: | Oxygen evolved; a glowing splinter of wood thrust into the mouth of the tube burns brilliantly. |

**15.** Some substances, which give no sublimate or gas in the matrass, are oxidized when heated in a hard glass tube, four inches long, open at both ends.

*Open tube.*

The tube is held at a slope of 45°, the substance being placed in it at one-third of the way from the lower end and gradually heated. When treated in this way the following bodies give characteristic reactions.

| SULPHUR AND SOME SULPHIDES: . . . | $SO_2$ is given off (§§194-198). |
| ARSENIC AND ARSENIDES: . . . . . | Sublimate of brilliant octahedral crystals of $As_2O_3$ (*vide* §§166 *et seq*). |
| ANTIMONY: . . . | Non-crystalline sublimate of $Sb_2O_3$ and $Sb_2O_4$ (*vide* §174). |
| BISMUTH: . . . . | Sublimate near the substance, fusible to brown globules. |
| MERCURIC SULPHIDE: | Sublimate of mercury, $SO_2$ being evolved at the same time. |

### SOLUTION AND PRECIPITATION.

**16.** Most substances if left in contact with water will dissolve to a greater or less extent. Those substances which require a relatively very large amount of water for their solution are called *insoluble*, those which dissolve more freely are termed *soluble*.

*Solubility*

No absolute line can be drawn between soluble and insoluble substances. Barium sulphate, which will dissolve in 87,000 times its weight of water, is commonly termed insoluble; while calcium sulphate, which dissolves in 400 times its weight, is termed difficultly soluble. When a solvent has taken up all that it will of a substance, the resulting solution is said to be *saturated*.

The limit of saturation depends upon the temperature. Almost all substances are more soluble at higher than at lower temperatures.

**17.** When two solutions are mixed together and produce, Precipita- by chemical change, an insoluble compound, the latter will tion. appear as a *precipitate*. Most precipitates, if abundant, will soon settle to the bottom of the solution, leaving the latter clear. If the precipitate is in very small quantity or in a very fine state of division, it may remain suspended for a long time Suspend- in the solution, and will then only appear as an opalescence. ed precipi- It may be said in general, that when a solution is not perfectly tates. clear and transparent, it contains a precipitate. It will readily be appreciated that the degree of dilution of a solution has a great deal to do with the appearance of any precipitate which Effect of may be formed. In most cases it is possible to dilute the solu- dilution. tion with so much water that the precipitate will be invisible or will not be formed at all. It is advisable, in order to become acquainted with each precipitate under varying condi- tions, for the student to execute each precipitative reaction in a highly dilute and also in a more concentrated solution.

## FILTRATION.

**18.** For the purpose of separating a solution from the pre- cipitate formed in it, the operation of filtration is resorted to. Filtration. A filter paper should be carefully folded, pressed in the fun- nel, and moistened, so as to adhere so closely to the funnel as to admit no air down the sides. Solutions filter much more rapidly when hot than when cold.

**19.** In order to remove the whole of the solution adhering Washing to a precipitate, the latter is to be washed, by directing a of precipi- stream from the wash-bottle around the upper edge of the tates. filter, until it is full. When this water has all run through, the operation is to be repeated as often as may be necessary. In Tests for order to determine when the operation is completed, catch a comple- few drops of the filtrate upon a perfectly clean piece of plati- tion of num foil and evaporate cautiously over a small Bunsen flame. washing. If no residue is left upon the foil, the washing is complete,

the temperature.
at higher than at

gether and produce,
ound, the latter will
es, if abundant, will
, leaving the latter
quantity or in a very
nded for a long time
r as an opalescence.
ution is not perfectly
tate.  It will readily
n of a solution has a
ny precipitate which
ble to dilute the solu-
itate will be invisible
dvisable, in order to
under varying condi-
eciptative reaction in
trated solution.

olution from the pre-
tration is resorted to.
d, pressed in the fun-
osely to the funnel as
ons filter much more

the solution adhering
shed, by directing a
he upper edge of the
as all run through, the
may be necessary.  In
is completed, catch a
y clean piece of plati-
a small Bunsen flame.
washing is complete,

otherwise not.  Sometimes other methods are employed for
ascertaining when the washing is finished.  These will be speci-
fied in their proper connection.  Never omit to assure your-
self that the washing is thoroughly done.

### EVAPORATION AND CRYSTALLIZATION.

**20.**  When water is removed from a solution, the limit of
solubility of the substance dissolved will be reached.  At this
point the latter will separate, very often in the form of crystals.
The most common way of removing the water is by means of
evaporation.  Evaporation may be effected: first, by simply Crystalli-
exposing the solution to the air at ordinary temperatures, in zation by
which case the evaporation is called spontaneous; second, by evapora-
warming the solution in an open vessel on a sand or water tion.
bath; third, by direct boiling.  The formation of crystals is an
operation that demands time, and we accordingly find that
slow evaporation produces larger and more perfect crystals,
than rapid.

If water be saturated with a crystalline solid (copper sul-
phate for example), at a high temperature and then cooled, a Crystalli-
portion of the substance will usually crystallize out, the amount zation by
depending on the difference in solubility of the body at the cooling.
two temperatures.

Crystallization is to be regarded as a particular case or form
of precipitation.  It is the process most often resorted to for
the purification of many chemical reagents.

### USE OF TEST PAPERS.

**21.**  Two kinds of test paper, litmus and turmeric, are
chiefly employed for ascertaining the *reaction* of a solution. Litmus
Litmus paper is turned red by substances which have an acid paper.
reaction.  Among these are most free acids, many normal Acid reac-
salts, such as aluminium sulphate, copper sulphate, etc., etc., tion.
and many acid salts such as $KHSO_4$.

**22.**  Reddened litmus paper is turned blue by substances Alkaline
which have an alkaline reaction, such as ammonia, and the reaction.
hydrates of sodium, potassium, calcium, barium, strontium,

magnesium and lead, and by the carbonates of ammonium, sodium, potassium and calcium.

**Reaction of hydrates and carbonates.** The yellow color of turmeric paper is turned to brownish red by substances having an alkaline reaction, such as ammonia, and the hydrates of sodium, potassium, calcium, barium and strontium, and by the normal carbonates of sodium, $Na_2CO_3$, and potassium, $K_2CO_3$.

**23.** Sodium bicarbonate, $NaHCO_3$, and potassium bicarbonate, $KHCO_3$, give no alkaline reaction with turmeric paper when pure, but do so with reddened litmus. By this means we may detect very small quantities of $Na_2CO_3$ or $K_2CO_3$, when mixed with $NaHCO_3$, or $KHCO_3$.

**Reaction of bicarbonates.**

**24.** Other colored test papers besides these are sometimes employed for detecting the acidity or alkalinity of solutions.[1] The most important of these is lacmoid paper. This closely resembles litmus, it being turned red by acids and blue by alkalies. It differs from litmus paper in the fact that it is not reddened by the normal salts referred to in §21.

---

[1] Among these may be mentioned—
Congo paper, blue with acids, red with alkalies.
Haematoxylin, yellow with acids, violet with alkalies.
Aurin, yellow with acids, red with alkalies.

s of ammonium,

urned to brownish
reaction, such as
otassium, calcium,
oonates of sodium,

d potassium bicar-
ith turmeric paper
. By this means
$Na_2CO_3$ or $K_2CO_3$,

hese are sometimes
inity of solutions.[1]
per. This closely
acids and blue by
e fact that it is not
§21.

# CHAPTER II.

### REACTIONS OF THE BASES.

#### SYNOPSIS OF THE CLASSIFICATION OF THE BASES.

**25.** The more commonly occurring bases are divided into six groups, according to the behavior of their solutions to the group-reagents, hydrogen sulphide, ammonium sulphide and ammonium carbonate.

<div style="float:right">Group reagents.</div>

| | | |
|---|---|---|
| GROUP VI. | TIN, ANTIMONY, ARSENIC, GOLD, PLATINUM. | Precipitated as sulphides by hydrogen sulphide, from acidified solutions. The precipitate is *soluble* in yellow ammonium sulphide. |
| GROUP V. | SILVER, MERCURY, BISMUTH, LEAD, COPPER, CADMIUM. | Precipitated as sulphides .om acidified solutions. The precipitate is *insoluble* in yellow ammonium sulphide. |
| GROUP IV. | COBALT, NICKEL, IRON, MANGANESE, ZINC. | Precipitated from neutral or alkaline solutions by hydrogen sulphide or ammonium sulphide, as sulphides. Not precipitated by hydrogen sulphide from acidified solutions. |

| | | |
|---|---|---|
| GROUP III. | ALUMINIUM, CHROMIUM, (BERYLLIUM). | Not precipitated as sulphides, from either acid or neutral solutions, by hydrogen sulphide or ammonium sulphide. Precipitated as hydrates by ammonia or ammonium sulphide. |
| GROUP II. | BARIUM, CALCIUM, STRONTIUM, (MAGNESIUM). | Not precipitated by hydrogen sulphide, ammonium sulphide or ammonia. Precipitated as carbonates from neutral solutions by ammonium carbonate. |
| GROUP I. | POTASSIUM, SODIUM, AMMONIUM. | Not precipitated by either of the foregoing group-reagents. |

## GROUP I.

### SODIUM, POTASSIUM, AMMONIUM.

**26.** The bases of the first group are distinguished by the almost universal solubility of their compounds. Their hydrates, carbonates and sulphides are soluble in water, to which they impart an alkaline reaction.

#### SODIUM, Na'

**27.** Metallic sodium exhibits on a fresh cut surface a metallic lustre, which quickly tarnishes when exposed to moist air. It reacts vehemently with water, liberating hydrogen
NaOH. and forming sodium hydrate, a caustic deliquescent solid, which exhibits an alkaline reaction even in highly dilute solutions.

**28.** Sodium compounds are somewhat volatile at the temperature of the Bunsen flame, to which they impart an

intense yellow color (§7). This is an extraordinarily sensitive reaction, by means of which sodium may be detected in dust, perspiration and most natural products. Its great sensitiveness makes it necessary to observe special caution in the application of this test, since sodium, when present only in minute traces as an accidental impurity, may, otherwise, be taken for an essential constituent. *Flame reaction of sodium.*

**29.** Some silicates containing sodium are volatile with difficulty, and exhibit the reaction well, only when finely pulverized and moistened with sulphuric acid before being introduced into the flame. *Detection of Na in silicates.*

**30.** Sodium chloride, when treated with platinum chloride, forms sodium chloro-platinate, $Na_2PtCl_6$, a soluble salt, which on cautious evaporation of the solution appears as long, prismatic, yellow crystals, easily distinguishable from the corresponding potassium and ammonium salts. (See below.) *Reaction with $PtCl_4$.*

### POTASSIUM, K ᴸ

**31.** Potassium oxidizes readily when exposed to moist air or oxygen. When thrown on water it liberates hydrogen, which burns with a characteristic violet flame, potassium hydrate being formed. *Metallic potassium.*

$$K + H_2O = KOH + H$$

Potassium hydrate is a very soluble, deliquescent, caustic solid with a strong alkaline reaction. It decomposes the salts of most metals, forming hydrates, which in some cases are soluble in an excess. *KOH.*

**32.** Most potassium compounds are volatile at the temperature of the Bunsen flame, to which they impart a violet color. Nearly all the salts of this metal are readily soluble in water, exceptions being the acid potassium tartrate, $KHC_4H_4O_6$, and potassium chloro-platinate, $K_2PtCl_6$. *Flame test for K.*

**33.** If a potassium salt, (especially KCl), in moderately concentrated solution, be treated with hydrochloric acid and platinum chloride, a crystalline, yellow precipitate of potassium chloro-platinate, $K_2PtCl_6$, appears either at once or after standing some time. Under the microscope this precipitate is seen *Precipitation of $K_2PtCl_6$.*

to consist of octahedral crystals.   It is somewhat soluble in water and the addition of an equal bulk of alcohol to the solution makes the reaction more delicate,   Salts of all other bases, excepting sodium and magnesium, should be absent when this test is applied.

**34.**   If sodium tartrate or free tartaric acid be added to a moderately concentrated neutral solution of a potassium salt and the mixture then strongly acidified with acetic acid, a crystalline precipitate of acid potassium tartrate, $KHC_4H_4O_6$ will form on standing.

$KHC_4H_4O_6$, "Cream of Tartar."

Violent agitation facilitates the formation of this precipitate and the addition of alcohol, in bulk equal to the solution, makes the test more delicate.  Sodium salts give no precipitate with tartaric acid.

**35.**   The violet color which potassium compounds impart the Bunsen flame is usually used as a test, which is, however, not very delicate although characteristic.  All other substances which color the flame must be absent.  Magnesium and ammonium compounds do not interfere.  If sodium is present, the flame must be observed through one, two or three thicknesses of cobalt glass.  This blue glass, if used in sufficient thickness, completely shuts off the yellow sodium light but allows the potassium flame to shine through, with a somewhat reddish tinge.

Detection of potassium by flame test in presence of sodium.

### AMMONIUM, $(NH_4)^{I.}$

**36.**   Ammonia $(NH_3)$ is a pungent gas, highly soluble in water, to which it imparts its characteristic odor and basic properties.

Salts of $NH_4$.

It combines with acids directly to form salts of the hypothetical radical ammonium, $(NH_4)$, for example

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

Ammonium salts are odorless, ammonium carbonate being an exception, and usually soluble in water.

Decomposition of $NH_3$ compounds by heat.

**37.**   Ammonium salts are decomposed and volatilized at a temperature below redness.   They may be oxidized and removed from a concentrated solution by continued boiling with an excess of concentrated nitric acid, followed by evapo-

The left partial column (cut off):

[§37

omewhat soluble in
 of alcohol to the
, Salts of all other
, should be absent

acid be added to a
of a potassium salt
with acetic acid, a
tartrate, $KHC_4H_4O_6$

n of this precipitate
qual to the solution,
s give no precipitate

m compounds impart
t, which is, however,
All other substances
Magnesium and am-
sodium is present, the
o or three thicknesses
in sufficient thickness,
ght but allows the pot-
mewhat reddish tinge.

t.

gas, highly soluble in
eristic odor and basic

rm salts of the hypo-
example
$H_4)_2SO_4$
onium carbonate being
ter.

osed and volatilized at
may be oxidized and
by continued boiling
cid, followed by evapo-

---

ration to dryness.  They should be removed before applying the tests for potassium mentioned in §§33 or 34.

**38.**  If an ammonium salt be rendered alkaline with sodium or potassium hydrate and warmed, ammonia will be set free or potassium hydrate and warmed, ammonia will be set free and may be perceived by its characteristic odor and alkaline reaction.  To observe the latter, cut a slit in a cork fitting the test tube which contains the ammonium salt and potassium hydrate.  Suspend a narrow strip of red litmus paper from the slit of the cork, and set the latter loosely in the test tube, in such a way that it will hang freely *without touching the sides, or the liquid.*  If it turns blue, ammonia is present. *Decomposition by alkalies.*

$$NH_4Cl + KOH = KCl + NH_3 + H_2O$$

**39.**  Ammonium chloride gives, with hydrochloric acid and platinum chloride, a reaction similar to that of the potassium salts; the precipitate being, in this case, ammonium chloro-platinate, $(NH_4)_2PtCl_6$, indistinguishable from potassium chloro-platinate (§33). *Ammonium chloro-platinate.*

**40.**  Nessler's reagent, a solution of mercuric iodide with an excess of potassium hydrate (see table of reagents), produces in very dilute solutions of ammonia or ammonium salts, a reddish brown coloration or precipitate.  This reaction is adapted to the detection of minute traces of ammonia, such, for example, as those which are often found in contaminated drinking water.  (See Special Part, §332). *Nessler's test for $NH_3$.*

## GROUP II.

### CALCIUM, BARIUM, STRONTIUM, (MAGNESIUM).

**41.**  The bases of the second group are distinguished from those of the first, by the fact that their normal carbonates and phosphates are insoluble in water.  They are distinguished from those of groups III, IV, V, and VI by the fact that dilute solutions of their salts are not precipitated either by ammonia, ammonium sulphide or hydrogen sulphide. *Characteristics of salts of Ca, Ba, Sr and Mg.*

**42.**  Ammonium carbonate, when added to a neutral solution, will precipitate all the bases of this group as carbonates.  The precipitation of magnesium carbonate is incomplete and *Precipitation of $CaCO_3$, $BaCO_3$, and $SrCO_3$*

may be entirely prevented by the addition of a sufficient quantity of ammonium chloride. The precipitated carbonates may be pasty at first, but by gently warming the solution in which they are formed, they gradually become granular. In this condition, they subside and filter more readily.

### CALCIUM, Ca$^{II}$.

Ca, flame reaction.
**43.** Calcium compounds, especially the salts of calcium with the haloid acids, $CaCl_2$ etc., impart an orange or orange-red color to the Bunsen flame.

$CaSO_4 +$ $2H_2O$.
**44.** Solutions of calcium salts give, with sulphuric acid or a soluble sulphate, a crystalline precipitate of calcium sulphate, $CaSO_4,2H_2O$, (gypsum). Since this precipitate is somewhat soluble in water, it will only appear in moderately concentrated solutions.

Ca precipitated by sodium phospate.
**45.** Sodium phosphate, $Na_2HPO_4$, when added to an alkaline solution of a calcium salt, produces a flocculent precipitate of tri-calcium phosphate, $Ca_3(PO_4)_2$, soluble in acids, even in dilute acetic.

Oxalate test for Ca.
**46.** Neutral or alkaline solutions of calcium salts give, with ammonium oxalate, even in highly dilute solutions, a micro-crystalline precipitate of calcium oxalate, $CaC_2O_4 + 2H_2O$ insoluble in dilute acetic acid or in ammonia, soluble in the mineral acids.

### STRONTIUM, Sr$^{II}$.

Sr, flame reaction.
**47.** Strontium compounds, especially salts of the haloid acids, ($SrCl_2$ etc.), impart an intense crimson color to the flame.

**48.** Solutions of strontium salts give, with sulphuric acid or soluble sulphates (including calcium sulphate), a micro-crystalline precipitate of strontium sulphate, $SrSO_4$.

Strontium sulphate.
In highly dilute solutions, this precipitate only appears on standing some time. The reaction with calcium sulphate solution (which of course cannot precipitate a calcium salt) serves to distinguish solutions of strontium from those of calcium compounds.

on of a sufficient
pitated carbonates
g the solution in
ome granular. In
readily.

salts of calcium
art an orange or

h sulphuric acid or
of calcium sulphate,
ipitate is somewhat
moderately concen-

n added to an alka-
locculent precipitate
ble in acids, even in

calcium salts give,
dilute solutions, a
ate, $CaC_2O_4+2H_2O$
monia, soluble in the

salts of the haloid
crimson color to the

, with sulphuric acid
sulphate), a micro-
te, $SrSO_4$.

itate only appears on
ith calcium sulphate
itate a calcium salt)
ntium from those of

**49.** Sodium phosphate reacts with strontium as it does with calcium compounds (§45). — *Strontium phosphate.*

**50.** Ammonium oxalate reacts with strontium as it does with calcium compounds. The precipitate is not quite so insoluble. — *Strontium oxalate.*

### BARIUM, Ba II.

**51.** Barium compounds impart to the flame a leaf-green coloration, which often appears only after the platinum wire has been held in the flame for some time. Barium sulphate and the haloid salts exhibit this reaction well. — *Ba flame test.*

**52.** Sulphuric acid or a soluble sulphate produces, even in the most highly dilute, acid or alkaline solutions of barium, a very finely divided precipitate of barium sulphate, $BaSO_4$. When calcium sulphate is used for this test, the precipitate appears at once (distinction from strontium). — $BaSO_4$.

**53.** Sodium phosphate reacts with barium as it does with calcium compounds (§45). — $Ba_3(PO_4)_2$.

**54.** Ammonium oxalate reacts with barium as it does with calcium compounds. The precipitate, $BaC_2O_4$, is not quite so insoluble. — $BaC_2O_4+2H_2O$.

**55.** Potassium chromate, $K_2CrO_4$, or potassium pyrochromate, $K_2Cr_2O_7$, produces, in a neutral solution of barium salts, a yellow, finely crystalline precipitate of barium chromate, $BaCrO_4$; insoluble in ammonia, nearly insoluble in dilute acetic acid, more readily soluble in dilute mineral acids. Dilute solutions of strontium, calcium and magnesium salts give no precipitate with these reagents. — *Precipitation of $BaCrO_4$ distinguishes Ba from all other bases of Group II.*

### MAGNESIUM, Mg II.

**56.** Solutions of magnesium salts, *when free from ammonium salts*, give, on treatment with sodium, potassium, or ammonium carbonate, an amorphous precipitate of magnesium carbonate, $MgCO_3$. Since this precipitate is soluble in solutions of ammonium salts, it does not appear when the latter are present in sufficient quantity. — $MgCO_3$.

**57.** If therefore we add to a neutral solution of a magne-
Separation sium salt, first, ammonium chloride and, then, ammonium
of Mg carbonate, no precipitate will appear. *This reaction serves to*
from *distinguish magnesium salts and to separate them from those of*
Ba, Ca, Sr. *the other bases of this group.*

**58.** Magnesium compounds impart no color to the flame.

**59.** The addition of ammonia to a solution of a magnesium
salt precipitates magnesium hydrate.

This precipitation is incomplete and is entirely prevented by
ammonium chloride or other ammonium salts. A similar pre-
$Mg(OH)_2$. cipitation is produced by the hydrates of sodium, potassium,
barium, or calcium, being nearly complete in this case, in the
absence of ammonium salts or when the alkaline solution is
boiled until all ammonia is expelled. Magnesium hydrate may
be dissolved in a solution of ammonium chloride.

*a.* Many compounds of magnesium (such as chloride,
Blowpipe sulphate, carbonate, hydrate, nitrate), if strongly ignited and
test for then moistened with cobalt nitrate solution and again ignited,
Mg. exhibit a rose or pink coloration.

$MgSO_4$ **60.** Magnesium salts give no precipitate with sulphuric
is soluble. acid or with soluble sulphates.

**61.** If a magnesium salt, in neutral solution, be treated
with ammonium chloride, sodium phosphate and with ammo-
nia, in large excess, a crystalline precipitate will appear, of
Precipita-
tion of magnesium ammonium phosphate, $MgNH_4PO_4$, soluble in
$MgNH_4PO_4$ dilute acids, slightly soluble in water, insoluble in ammonia
water.

$$MgCl_2 + NH_3 + NH_4Cl + Na_2HPO_4 =$$
$$2NaCl + NH_4Cl + MgNH_4PO_4$$
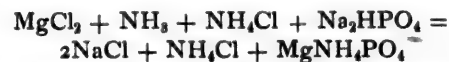
If the solution is dilute, this precipitate does not appear at
once. Its formation is aided by violent shaking. If the inside
$MgNH_4PO_4$ of the glass tube be rubbed with a glass rod, the precipitate
must be will form at and adhere to the rubbed places, so that visible
crystalline. lines may, in this way, be drawn upon the glass. In applying
this test, the appearance of a non-crystalline precipitate is not
to be regarded as indicative of magnesium. Sometimes the
precipitate, when first formed, will not be crystalline, but will
become so on standing over night in a warm place.

## GROUP III.

### ALUMINIUM AND CHROMIUM.

**62.** The bases of this group are completely precipitated from their solutions by ammonia, ammonium carbonate or ammonium sulphide, as hydrates. Their solutions are not precipitated by hydrogen sulphide.

### ALUMINIUM, Al $^{\mathrm{III}}$.

**63.** Aluminium is a bluish white metal, which dissolves readily in hydrochloric acid, forming aluminium chloride. It is soluble with difficulty in most oxy-acids. Solutions of its normal salts have a strongly acid reaction and are more or less decomposed, on boiling, into free acid and basic salt. <span style="float:right">Al.</span>

**64.** Ammonia produces in a solution of an aluminium salt a colorless, amorphous, flocculent, or semi-gelatinous, precipitate of aluminium hydrate, $Al(OH)_3$, which is soluble in dilute acids and nearly insoluble in dilute ammonia.[1] This precipitate is so transparent that small quantities of it may readily be overlooked. On standing, it gathers into larger flocks and may then be more easily seen. <span style="float:right">Al(OH)₃.</span>

After washing and drying, it can be converted, by heating to bright redness on platinum foil, into alumina, $Al_2O_3$. The latter compound, if moistened with a dilute solution of cobalt nitrate and again heated in the oxidizing flame, turns light blue, a useful and characteristic reaction. <span style="float:right">Cobalt solution test for Al₂O₃.</span>

**65.** Sodium hydrate, when added to the solution of an aluminium salt causes the precipitation of aluminium hydrate, which readily dissolves in an excess of the precipitant, forming the soluble compound, sodium aluminate, $Al(ONa)(OH)_2$. <span style="float:right">Aluminates.</span>

Potassium hydrate gives a precisely similar reaction.

**66.** A solution of an aluminate, upon exact neutralization with an acid, or upon addition of an excess of ammonium chloride, gives a precipitate of aluminium hydrate. <span style="float:right">Precipitation by NH₄Cl of Al(OH)₃.</span>

$$Al(ONa)(OH)_2 + HCl = Al(OH)_3 + NaCl$$
$$Al(ONa)(OH)_2 + NH_4Cl = Al(OH)_3 + NaCl + NH_3$$

---
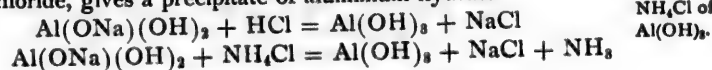
[1] L. Blum, *Fres. Zeitschrift:* **27**, p. 19.

**67.** A solution of an aluminium salt containing but little free acid, if treated with an excess of ammonium or sodium acetate, forms aluminium acetate, which on boiling is decomposed, forming basic aluminium acetate, which appears as a colorless, amorphous precipitate.

Basic acetate.

$$Al(OCOCH_3)_3 + H_2O = AlO(OCOCH_3) + 2HOCOCH_3$$

### CHROMIUM, Cr III & VI.

**68.** Chromium is a brittle, white, extremely hard metal, easily soluble in hydrochloric acid, with difficulty in dilute sulphuric, and insoluble in nitric acid. Its salts are all colored, being usually violet or green, less often red. Their solutions, when boiled, undergo a similar, partial decomposition to those of aluminium.

Cr salts.

**69.** Ammonia produces, in solutions of chromium salts, a flocculent or semi-gelatinous apple-green precipitate of chromium hydrate, $Cr(OH)_3$, which is insoluble in dilute ammonia, soluble in acids. When ignited, chromium hydrate loses water, being converted into deep green chromium oxide, $Cr_2O_3$.

Cr(OH)₃.

**70.** Sodium hydrate produces, in solutions of chromium salts, a precipitate of chromium hydrate, which readily dissolves in an excess of the precipitant, sodium chromite, $Cr(OH)_2ONa$, being formed. The latter solution is decomposed on boiling, a sage-green precipitate of hydrated chromium oxide, probably $CrOOH$, appearing. Potassium hydrate reacts in a precisely similar way.

Alkaline Cr solutions.

This re-precipitation from alkaline solutions, on boiling, may be used for the separation of aluminium and chromium, since the former remains in solution, while the latter is precipitated.

**71.** The oxide, hydrate, or salts of chromium, may be converted into chromic acid by powerful oxidizing agents. If chromium hydrate or a chromium salt is warmed with strong nitric acid and potassium chlorate, the green color of the mixture will change to reddish yellow, in consequence of the formation of chromic acid.

Oxidation to H₂CrO₄.

$$2Cr(OH)_3 + 3O = 2H_2CrO_4 + H_2O$$
$$Cr(SO_4)_3 + 3O + 5H_2O = 2H_2CrO_4 + 3H_2SO_4$$
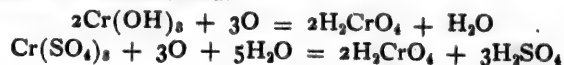
ntaining but little
onium or sodium
boiling is decom-
hich appears as a

) + 2HOCOCH₃

emely hard metal,
difficulty in dilute
alts are all colored,
. Their solutions,
omposition to those

f chromium salts, a
precipitate of chro-
e in dilute ammonia,
hydrate loses water,
oxide, $Cr_2O_8$.
utions of chromium
which readily dis-
sodium chromite,
r solution is decom-
e of hydrated chro-
Potassium hydrate

lutions, on boiling,
ium and chromium,
while the latter is

chromium, may be
oxidizing agents. If
warmed with strong
green color of the
consequence of the

$O_4 + H_2O$
$CrO_4 + 3H_2SO_4$

Similarly, a chromium salt or $Cr(OH)_3$, may be converted into a chromate by fusion with potassium nitrate and sodium carbonate.

$$Cr_2(SO_4)_3 + 5Na_2CO_3 + 3KNO_3 =$$
$$3Na_2SO_4 + 2Na_2CrO_4 + 3KNO_2 + 5CO_2$$
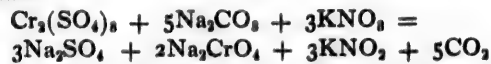
*a.* To effect this change, mix the chromium compound with about ten parts of sodium carbonate and one part of potassium nitrate. Fuse the mass for five minutes on platinum foil. Dissolve the product in water. Its intense yellow color shows the presence of a chromate, and therefore of a chromium compound in the original substance. Acidify this solution with acetic acid and then add lead nitrate, when a yellow precipitate of lead chromate will be formed (*v.* §221). <span>Confirmatory test for Cr compounds.</span>

This confirmatory test should never be omitted, since the yellow color of chromic acid and of chromates is much more intense and more characteristic than the green color of the chromium salts.

**72.** Chromium compounds give a green color to the borax bead in oxidizing and reduction flames (§7). <span>Cr in the borax bead.</span>

**73.** A solution of a chromium salt containing but little free acid, if treated with an excess of ammonium or sodium acetate, forms chromium acetate, which, on boiling, is decomposed, forming basic chromium acetate, which appears as an apple-green, amorphous precipitate. <span>Basic acetate.</span>

$$Cr(OCOCH_3)_3 + H_2O = CrO(OCOCH_3) + 2HOCOCH_3$$
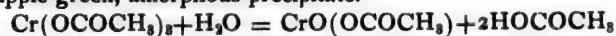
### GROUP IV.
### COBALT, NICKEL, IRON, MANGANESE AND ZINC.

**74.** Bases of this group give, with ammonium sulphide in neutral or alkaline solutions, a precipitate of the corresponding sulphides. In acid solutions they give no precipitate with hydrogen sulphide. They are precipitated by sodium carbonate as carbonates or basic carbonates.

#### COBALT, Co = 59.

**75.** Cobalt is a white, magnetic metal, which dissolves readily in dilute acids to form cobaltous salts, the solutions of which are red, although the anhydrous salts are blue or violet. <span>Co salts.</span>

**76.** Neutral solutions of cobaltous salts give, with ammo-
CoS.    nium sulphide, a black precipitate of cobaltous sulphide, CoS,
insoluble in cold, dilute hydrochloric acid.

**77.** Ammonia produces in cobaltous solutions a blue pre-
Co(OH)₂. cipitate of cobaltous hydrate, soluble in an excess of ammonia.
Ammonium salts prevent the formation of this precipitate.

Borax   **78.** Borax dissolves cobalt compounds, in either oxidizing
bead reac- or reducing flame, to a deep blue bead (§9).
tion.

**79.** Cobalt compounds, when heated on charcoal with
sodium carbonate, in the reducing flame, are reduced to
Reduction metallic cobalt, which appears in the form of magnetic particles
on char- when the fused mass is treated with water (§12).
coal of Co.

**80.** When a cobalt solution is mixed with potassium nitrite
in excess and then strongly acidified with acetic acid, the cobalt
Reaction separates, after standing for some time in a warm place, as a
with     canary-yellow, crystalline precipitate of tri-potassium cobaltic
KNO₂.    nitrite, $K_3Co(NO_2)_6$.

## NICKEL, Ni II & III.

**81.** Nickel is a silvery white, magnetic metal, which dis-
Salts of solves readily in warm dilute acids, forming green nickelous
Ni.      salts, which are usually yellow when anhydrous.

**82.** The addition of ammonium sulphide, to a neutral or
an alkaline solution of nickel salts, produces a black precipitate
Precau-  of nickel sulphide, NiS, insoluble in cold, dilute hydrochloric
tions in acid. This precipitate is somewhat soluble in an excess of
the precip- ammonium sulphide and ammonia, the solution having a
itation of brownish color. An excess of the precipitant should be
NiS.     avoided. The addition of ammonium chloride aids the com-
plete precipitation.

**83.** Ammonia produces, in solutions of nickel salts, a green
Ni(OH)₂. precipitate, which dissolves very readily in an excess of ammo-
nia, giving a deep blue solution.

**84.** Borax dissolves nickel compounds in the oxidizing
Borax   flame to a clear brown bead (violet while hot), which, in the
bead    reducing flame, becomes gray and then colorless.
reaction.

give, with ammo-
ous sulphide, CoS,

lutions a blue pre-
excess of ammonia.
his precipitate.
in either oxidizing
).

on charcoal with
, are reduced to
f magnetic particles
(§12).

th potassium nitrite
cetic acid, the cobalt
a warm place, as a
-potassium cobaltic

ic metal, which dis-
ing green nickelous
drous.

ide, to a neutral or
s a black precipita·e
, dilute hydrochloric
uble in an excess of
solution having a
recipitant should be
loride aids the com-

of nickel salts, a green
h an excess of ammo-

nds in the oxidizing
le hot), which, in the
colorless.

**85.** Nickel compounds, when heated on charcoal with sodium carbonate in the reducing flame, are reduced to metallic nickel, which appears in the form of magnetic spangles when the fused mass is treated with water. *Reduction on charcoal of Ni.*

**86.** Nickelous salts, when treated with potassium nitrite and acetic acid, as in §80, are not precipitated. *Difference of Ni from Co.*

### IRON, Fe II & III.

**87.** Iron dissolves in dilute acids, forming ferrous salts, which are usually colorless or pale green. They may be converted into ferric salts by treatment with boiling nitric acid, chlorine, bromine, or other oxidizing agents. *Salts of Fe, II, and Fe, III.*

Ferric solutions may readily be reduced to ferrous by treatment with hydrogen sulphide or other reducing agents.

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl$$
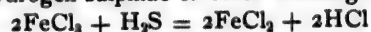
**88.** Borax dissolves iron compounds, in the oxidizing flame, to a clear bead, which is red while hot, yellow when cold. In the reducing flame the bead turns bottle-green. *Borax bead reaction.*

**89.** Iron compounds, when heated on charcoal with sodium carbonate in the reducing flame, are reduced to metallic iron, which appears in the form of magnetic particles when the fused mass is treated with water. *Reduction of Fe on charcoal.*

**90.** Solutions of ferrous or ferric salts give with ammonium sulphide a black precipitate of ferrous sulphide, FeS, readily soluble in cold, dilute hydrochloric acid. This precipitate, when exposed to the air in a moist condition, readily oxidizes to ferrous sulphate, etc. It should, therefore, be filtered and washed as rapidly as possible. *FeS.*

#### FERROUS SALTS.     *Fe II salts.*

**91.** Ammonia produces, in solutions of ferrous salts, a colorless precipitate of ferrous hydrate, which, by oxidation, very rapidly turns green, then black, finally reddish brown. The hydrates of sodium and potassium give a similar reaction. *Fe(OH)₂.*

**92.** A neutral or acid solution of a ferrous salt gives, with potassium ferricyanide, a deep blue precipitate of *Turnbull's blue*, the composition of which is variable. *Fe₃(CN)₁₂, Turnbull's blue.*

**93.** A neutral or acid solution of a ferrous salt gives, with potassium ferrocyanide, a pale blue precipitate, which rapidly turns deep blue.

**94.** An acidified solution of a ferrous salt is not altered by potassium sulphocyanate.

**Fe$^{III}$ salts.**

### FERRIC SALTS.

**95.** Solutions of normal ferric salts are usually yellow or red and have a distinctly acid reaction towards litmus paper.

Ammonia produces an amorphous, reddish brown precipitate of ferric hydrate, $Fe(OH)_3$, entirely insoluble in an excess of the precipitant.

$$FeCl_3 + 3H_2O + 3NH_3 = Fe(OH)_3 + 3NH_4Cl$$
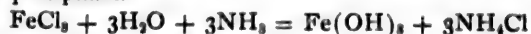
The hydrates of sodium or potassium give an exactly similar reaction.

**Fe(OH)$_3$.** Ferric hydrate is readily soluble in alkaline solutions which contain glycerine, sugar or tartaric acid; many other kinds of organic substances producing a similar effect.

**96.** A neutral or acid solution of a ferric salt gives, with potassium ferricyanide, a reddish brown coloration, but no precipitate.

**Ferric ferricyanide as a test for SO$_2$, etc.** This mixture is turned blue by many reducing agents, such as hydrogen sulphide, sulphurous acid, stannous chloride, metallic zinc, etc., and is often employed as a reagent to test for reducing agents. Paper dipped in this solution can be preserved in the dark and used as a test paper for reducing substances. It is called "blue paper" because it is turned blue by the light or by the compounds named.

**97.** A neutral or acid solution of a ferric salt gives, with potassium ferrocyanide, a blue coloration or a blue precipitate, consisting of *Prussian blue*. Its composition is variable.

**Prussian blue.** Prussian blue is insoluble in dilute nitric, hydrochloric or sulphuric acids, but dissolves in a concentrated solution of oxalic acid.

**Sulphocyanate test for Fe$^{III}$.** **98.** An acid solution of a ferric salt is turned blood-red by the addition of potassium sulphocyanate, a ferric potassium sulphocyanate being formed, of the composition, $Fe(SCN)_3$,

9KSCN. If this solution is shaken with a little ether, the latter will be colored red.

**99.** A solution of a ferric salt containing but little free acid, if treated with an excess of ammonium or sodium acetate, turns red, from the formation of ferric acetate, $Fe(OCOCH_3)_3$. If this solution is boiled, all the iron is thrown down as basic ferric acetate, a brick-red, flocculent precipitate of variable composition.

Basic acetate.

$$Fe(OCOCH_3)_3 + H_2O = FeO(OCOCH_3) + 2HOCOCH_3$$

**100.** If to a solution of a ferric salt, sodium phosphate be added in excess, and then ammonia, a white precipitate will be formed, of ferric phosphate, insoluble in alkalies and acetic acid, soluble in dilute mineral acids.

$FePO_4$.

$$FeCl_3 + Na_2HPO_4 + NH_3 = FePO_4 + 2NaCl + NH_4Cl$$

### MANGANESE, Mn II to VII.

**101.** Manganese is a brittle, gray metal, which oxidizes readily in the air and dissolves easily in dilute acids, forming manganous salts, which are usually flesh colored. The higher oxides of manganese, $Mn_2O_3$, $Mn_3O_4$, $MnO_2$, $Mn_2O_7$, etc., dissolve in warm hydrochloric acid, forming manganous chloride and free chlorine.

**102.** The addition of ammonium sulphide to a solution of a manganous salt precipitates manganous sulphide, $MnS,H_2O$. This precipitate is salmon colored, but turns dark upon exposure to the air. It is insoluble in alkalies and soluble in dilute acids. On heating, it sometimes turns green through loss of water, after which change, it has the composition represented by the formula, $MnS$.

MnS.

**103.** The addition of ammonia to a solution of a manganous salt throws down manganous hydrate, $Mn(OH)_2$, a white precipitate, which rapidly absorbs oxygen from the air and turns brown. If the solution contains much ammonium salt, ammonia produces no precipitate at first. Potassium and ammonium hydrates react in the same way as ammonia.

$Mn(OH)_2$.

**104.** The addition of chlorine or bromine water to a solution of manganous acetate throws down all the manganese, as hydrated manganese peroxide, $MnO(OH)_2$.

$MnO_2$.

**105.** Potassium ferrocyanide produces in manganese solutions a precipitate of manganese ferrocyanide.

Borax bead reaction.

**106.** Manganese compounds dissolve in the borax or metaphosphate bead (§18), rendering it violet in the oxidizing flame, colorless in the reducing flame.

$N_2MnO_4$.

$MnO_2$.

**107.** Manganese compounds when fused with a soda bead in the oxidizing flame, color it bright apple-green, from the formation of sodium manganate, $Na_2MnO_4$. If the bead be dissolved in water and then boiled with a drop of alcohol, brown flocks of manganese peroxide separate.

$HMnO_4$.

**108.** If a manganese compound be warmed with concentrated nitric acid and lead peroxide, $PbO_2$ (or a fragment of potassium chlorate), the solution will turn violet, from the formation of permanganic acid, $HMnO_4$. This reaction is extremely delicate.

### ZINC, $Zn^{II}$.

Blowpipe reactions of Zn.

**109.** Zinc is a white, crystalline metal, which dissolves slowly, when pure, in dilute acids, forming colorless salts which have an astringent taste. The metal, or its oxy-salts, when heated in the oxidizing flame, give a film of zinc oxide, $ZnO$, yellow when hot, white when cold. If this film be moistened with a dilute solution of cobaltous nitrate, and then intensely heated in the oxidizing flame, it becomes green.

$ZnS$.

**110.** Zinc is precipitated from solutions of its salts, on the addition of ammonium sulphide, a zinc sulphide, $ZnS$, a colorless, pasty, flocculent or gelatinous precipitate, which is readily soluble in cold and dilute acids, except acetic, insoluble in ammonia and the alkalies.

Zinc sulphide gives the blowpipe reactions described in the foregoing paragraph.

$Zn(OH)_2$.

**111.** Ammonia, potassium hydrate and sodium hydrate produce, in solutions of zinc salts, a colorless, amorphous precipitate of zinc hydrate, $Zn(OH)_2$, which very readily dissolves in an excess of the precipitant. The addition of ammonium sulphide, or hydrogen sulphide, to such an alkaline solution, precipitates the zinc as zinc sulphide.

**112.** Potassium ferrocyanide, produces a white crystalline precipitate of zinc ferrocyanide $(Zn_3K_2Fe_2(CN)_{12})$, even in very dilute solutions of zinc salts.

### GROUP V.

### SILVER, MERCURY, LEAD, COPPER, BISMUTH, CADMIUM.

**113.** The bases of this group are precipitated by hydrogen sulphide from neutral, alkaline or slightly acid solution, as sulphides.

These sulphides are black, except cadmium sulphide, which is yellow, and are insoluble in ammonium sulphide. Sodium carbonate precipitates the bases of this group as carbonates or basic carbonates.

#### SILVER, $Ag^I$ or $(Ag_2)^{II}$.

**114.** Silver is insoluble in dilute sulphuric or hydrochloric acids, soluble in nitric acid, and in hot, concentrated sulphuric acid, forming colorless salts. <span style="float:right">Solubility of Ag.</span>

**115.** Solutions of a silver salt give with hydrogen sulphide a black precipitate of silver sulphide, $Ag_2S$; insoluble in dilute acids and alkalies; soluble, with decomposition, in boiling concentrated nitric acid. On charcoal it is readily reduced (§12). <span style="float:right">$Ag_2S$.</span>

**116.** Solutions of silver salts are thrown down by hydrochloric acid, or a soluble chloride, as silver chloride, $Ag_2Cl_2$,[1] a white, curdy precipitate, the separation of which is facilitated by shaking and by acidification with nitric acid. It becomes violet or black when exposed to the light. It is insoluble in acids and in sodium or potassium hydrates, readily soluble in ammonia, and in solutions of sodium thiosulphate or potassium iodide. <span style="float:right">$Ag_2Cl_2$.</span>

From these solutions it may again be thrown down by the addition of nitric acid. When fused on charcoal with sodium carbonate (§12) it is readily reduced to globules of silver.

---

[1] Also written AgCl. It is not settled whether all the salts of silver contain the double atom, $(Ag_2)^{II}$, or not. Their formulas are so written in the text in order to exhibit more clearly their analogy with mercurous and cuprous salts.

Ag₃Br₃
and
Ag₂I₂.

**117.** For the reactions of silver salts with iodides and bromides see §§270, 273, 276.

Reduction.

**118.** All silver compounds are reduced readily to the metallic state, when fused on charcoal with sodium carbonate.

**119.** Silver solutions, when warmed with tartaric acid and ammonia, are reduced. The silver is deposited, partly in the form of a metallic mirror on the sides of the test tube, partly as a gray powder of finely divided metal.

Ag₂O.

**120.** The cautious addition of ammonia to the solution of a silver salt throws down a brown or black precipitate of silver hydrate, $Ag_2(OH)_2$, or silver oxide, $Ag_2O$; easily soluble in excess of ammonia.

### MERCURY, $Hg^{II}$ and $(Hg_2)^{II}$

**121.** Mercury is the only metal which is liquid at ordinary temperatures. It dissolves in concentrated, hot sulphuric acid, or in dilute nitric acid, forming colorless mercuric sulphate, or mercurous nitrate, respectively. Mercurous salts may be converted into mercuric salts by warming with con-

Salts of
Hg.

centrated nitric acid, or hydrochloric acid and potassium chloride.

$$Hg_2(NO_3)_2 + 3HNO_3 = 2Hg(NO_3)_2 + H_2O + N_2O_4$$

Many mercuric salts are decomposed by water, a basic salt (usually yellow) being formed and a part of the acid being set free.

$$3HgSO_4 + 2H_2O = Hg_3O_2SO_4 + 2H_2SO_4$$

All mercury salts are volatile at high temperatures.

$(Hg_2)^{II}$.

### MERCUROUS COMPOUNDS.

Precipita-
tion with
H₂S.

**122.** Hydrogen sulphide produces, in a solution of a mercurous salt, a black precipitate, consisting of mercuric sulphide mixed with metallic mercury.

$$Hg_2(NO_3)_2 + H_2S = HgS + Hg + 2HNO_3$$

Hg₂Cl₂.

**123.** A solution of a mercurous salt gives, with hydrochloric acid or a soluble chloride, a white, curdy precipitate of mercurous chloride, $Hg_2Cl_2$.

This precipitate does not change color upon exposure to the

light. It is insoluble in dilute acids, but soluble in concentrated, hot nitric acid.

$$Hg_2Cl_2 + 4HNO_3 = HgCl_2 + Hg(NO_3)_2 + H_2O + N_2O_4$$
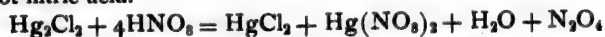
It is insoluble in ammonia, which turns it black.

### MERCURIC COMPOUNDS.                                    Hg II.

**124.**  Solutions of mercuric salts react with hydrogen sulphide, forming a black precipitate of mercuric sulphide, HgS, which is insoluble in boiling, concentrated nitric acid, but soluble in *aqua regia*.

HgS.

**125.**  The addition of a small amount of stannous chloride, $SnCl_2$, to a solution of a mercuric salt, produces a white, curdy precipitate of mercurous chloride (§123).

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

An *excess* of stannous chloride reduces the mercury to the metallic state, forming a grayish black precipitate.

$$HgCl_2 + SnCl_2 = SnCl_4 + Hg$$
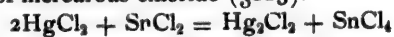
SnCl₂ and mercuric salts.
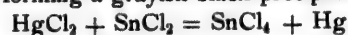
**126.**  If a drop of a mercuric solution be rubbed on a bright piece of copper, the latter will become covered with a silvery coating of mercury.

$$Hg(NO_3)_2 + Cu = Cu(NO_3)_2 + Hg$$

Mercurous solutions give a similar reaction.

If a drop of a mercury solution be placed upon a gold coin, and the gold be touched with a zinc rod immersed in the drop, metallic mercury will be deposited on the gold as a white stain.

Amalgamation test.

**127.**  If a mercuric compound be mixed with perfectly dry sodium carbonate, and strongly heated in a matrass (§14), a gray film will form in the upper part of the tube.  Under the microscope, this film may be seen to consist of globules of mercury.  If a fragment of iodine be then introduced half way down the tube, and gently warmed, the film will become bright red, from the formation of mercuric iodide.

Reaction with Na₂CO₃ in a matrass.

**128.**  Solutions of mecuric salts are not precipitated by hydrochloric acid.

### LEAD, Pb II & IV.

**129.**  Metallic lead is a very soft, bluish white metal, which dissolves in nitric acid to form lead nitrate, $Pb(NO_3)_2$.

Pb and its oxides.

The metal, when heated in an oxidizing flame, is converted into lead oxide, PbO, which appears as a brownish coating on the charcoal.

The higher oxides of lead, minium, $Pb_3O_4$, and lead peroxide, $PbO_2$, are decomposed by hydrochloric acid, chlorine being set free and lead chloride, $PbCl_2$, formed.

**PbS.**    **130.** Solutions of lead salts give a brownish black precipitate of lead sulphide, PbS, when treated with hydrogen sulphide. This precipitate is decomposed and dissolved by boiling, concentrated nitric acid.

**131.** Solutions of lead salts give with dilute sulphuric acid a white, micro-crystalline precipitate of lead sulphate, $PbSO_4$. This precipitate is very slightly soluble in water and dilute acids. It is readily soluble in a solution of the hydrates of sodium or potassium, or in a concentrated solution of ammonium acetate. It is blackened by ammonium sulphide and, on charcoal, it may readily be reduced to metallic lead. The precipitate does not appear in very highly diluted solutions.

**PbSO₄.**

**132.** The addition of hydrochloric acid to a concentrated lead solution produces a colorless, crystalline precipitate of lead chloride. This compound is moderately soluble in cold water, more readily in boiling water.

**PbCl₂.**

**133.** Potassium iodide produces in neutral lead solutions, which are not too dilute, a precipitate consisting of beautiful golden yellow spangles. This reaction is characteristic but not delicate.

**PbI₂.**

**134.** The addition of potassium chromate, $K_2CrO_4$, or pyrochromate, $K_2Cr_2O_7$, produces in neutral lead solutions, or in those which are acidified by acetic acid, a vivid yellow precipitate of lead chromate, $PbCrO_4$, which is somewhat soluble in dilute acids, nearly insoluble in acetic acid, and which is turned orange by ammonia.

**PbCrO₄.**

**135.** Lead compounds, when fused with sodium carbonate on charcoal in the reducing flame (§12), yield globules of metallic lead, which are readily recognized by their physical properties.

flame, is converted
rownish coating on

b₃O₄, and lead per-
loric acid, chlorine
rmed.

rownish black pre-
ated with hydrogen
d and dissolved by

dilute sulphuric acid
ad sulphate, $PbSO_4$.
in water and dilute
of the hydrates of
d solution of ammo-
um sulphide and, on
metallic lead. The
diluted solutions.

cid to a concentrated
alline precipitate of
ately soluble in cold

eutral lead solutions,
nsisting of beautiful
is characteristic but

hromate, $K_2CrO_4$, or
tral lead solutions, or
d, a vivid yellow pre-
is somewhat soluble
c acid, and which is

d with sodium carbon-
12), yield globules of
zed by their physical

### COPPER, Cu ᴵᴵ.

**136.** Copper is a soft metal of characteristic color, which on being heated in the air forms the black oxide, CuO. It is insoluble in dilute hydrochloric and sulphuric acids. It is readily oxidized, and then dissolved, by dilute nitric acid or by boiling concentrated sulphuric acid. Cupric salts containing water of crystallization are usually blue or green. Cuprous salts are generally colorless. They are not likely to be met with in an analysis, since they rapidly become oxidized, forming cupric salts; therefore only the latter will be considered here. *Solution of copper. Salts of copper.*

**137.** Hydrogen sulphide precipitates the copper from its salts as copper sulphide. *CuS.*

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

Copper sulphide is a brownish black precipitate, which is somewhat soluble in moderately concentrated hydrochloric acid, so that care should be taken to have the solution, from which copper sulphide is to be precipitated, only slightly acid. It dissolves readily in warm, concentrated nitric acid.

**138.** The addition of a little ammonia, to a solution of a copper salt, throws down copper hydrate, $Cu(OH)_2$, as a pale blue precipitate, which dissolves easily in an excess of ammonia to a deep blue solution. *$Cu(OH)_2$ dissolves in ammonia.*

**139.** Sodium or potassium hydrate throws down, from a solution of a copper salt a blue precipitate of copper hydrate, which is not soluble in an excess of the precipitant. If the sodium hydrate be added in excess, and the solution boiled, the precipitate changes into copper oxide, at the same time turning black. *Conversion of $Cu(OH)_2$ into CuO.*

**140.** Potassium ferrocyanide produces in neutral or acid solutions of copper salts, a brick-red precipitate, which consists of copper ferrocyanide, $Cu_2Fe(CN)_6$, or of copper potassium ferrocyanide, $Cu_3K_2Fe_2(Cu)_{12}$, according to the conditions of the precipitation. *Ferrocyanide test for Cu.*

**141.** If potassium iodide be added to a neutral or slightly acid solution of a copper salt, the solution will turn brown, *$Cu_2I_2$.*

from the separation of free iodine, a white precipitate of cuprous iodide appearing at the same time.

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2$$
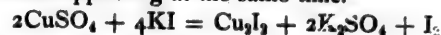
This reaction is not very delicate.

**142.** The addition of sulphurous acid (or a sulphite) and potassium sulphocyanate to the solution of a copper salt, $Cu_2(SCN)_2$. produces a curdy, white, amorphous precipitate of cuprous sulphocyanate, insoluble in dilute acids.

$$2CuCl_2 + 2KSCN + H_2SO_3 + H_2O =$$
$$Cu_2(SCN)_2 + H_2SO_4 + 2HCl + 2KCl$$
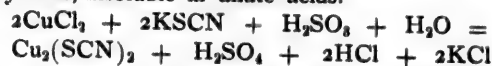
**143.** Globules of metallic copper are readily obtained, Reduction when a copper compound is reduced with sodium carbonate of Cu. on charcoal (§12, *see note*).

**144.** The borax bead is colored blue by copper com-Cu in the pounds in the oxidizing flame. In the reducing flame the borax bead. bead becomes red and opaque. The latter reaction is aided by the addition to the bead of a little stannic oxide, or tin foil.

**145.** Oxy-salts of copper impart to the flame an emerald-Flame green coloration. Haloid salts of the same metal color the coloration. flame blue.

Iron test **146.** A bright piece of steel or iron, when plunged into a for Cu. neutral or slightly acidified solution of a copper salt, becomes coated with metallic copper.

### BISMUTH, Bi ᴵᴵᴵ.

**147.** Bismuth is a brittle, reddish white metal, which, in $Bi_2O_3$. the oxidizing flame, is converted into bismuth oxide $Bi_2O_3$, which forms a yellow incrustation on the charcoal, brown while hot. It is insoluble in dilute hydrochloric and sulphuric acids, but soluble in dilute nitric acid. Normal bismuth salts Basic salts are readily decomposed by water, especially in boiling, form-of Bi. ing insoluble basic salts.

**148.** Hydrogen sulphide precipitates bismuth from its $Bi_2S_3$. solutions as bismuth sulphide, $Bi_2S_3$, insoluble in dilute acids, but readily dissolved, with decomposition, by boiling nitric acid.

**149.** If a bismuth solution, containing but little free acid, BiOCl.
be treated with a small quantity of hydrochloric acid, then
diluted with much water and boiled, a precipitate of bismuthyl[1]
chloride, $(BiO)Cl$, will be thrown down.

**150.** Ammonia, potassium hydrate, or sodium hydrate (BiO)OH.
throw down from bismuth solutions a white precipitate of bis-
muthyl hydrate, $(BiO)OH$, insoluble in alkalies.

**151.** Potassium pyrochromate precipitates bismuth chro- $Bi_2(CrO_4)_3$.
mate, $Bi_2(CrO_4)_3$, as a yellow powder, from bismuth solutions
which do not contain too much free acid. This precipitate
dissolves in dilute nitric acid.

**152.** If to a solution of bismuth, stannous chloride be
added and then sodium hydrate in excess, the bismuth will be $Bi_2O_2$.
thrown down as bismuthous oxide, $Bi_2O_2$, a black precipitate.
This is the best reaction for the detection of bismuth com-
pounds.

$$2Bi(NO_3)_3 + SnCl_2 + 8NaOH =$$
$$Bi_2O_2 + 6NaNO_3 + 2NaCl + Na_2SnO_3 + 4H_2O$$
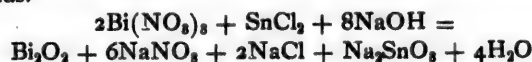
**153.** With sodium carbonate on charcoal, bismuth com- Reduction
pounds can be reduced before the blowpipe, to brittle globules of Bi.
of metallic bismuth.

**154.** If a bismuth compound be mixed with a little Blowpipe
sulphur and potassium iodide, and the mixture heated on char- test for Bi.
coal, a scarlet incrustation of bismuth iodide will be formed on
the support. The same reaction may with advantage be car-
ried out in the closed tube or matrass.

### CADMIUM, Cd �II.

**155.** Cadmium is a silvery white, malleable, volatile Cd.
metal, which readily burns in the oxidizing flame, forming
cadmium oxide, CdO, which produces a brown incrustation on
the support. The metal dissolves in dilute hydrochloric,
nitric, or sulphuric acids, forming colorless salts.

**156.** Hydrogen sulphide precipitates from solutions of
cadmium salts cadmium sulphide, CdS, as a bright yellow CdS.

---

[1] The univalent radical (BiO)' which occurs in many compounds, is called
*bismuthyl.*

precipitate, which is insoluble in cold, dilute acids, and in
potassium cyanide. It is readily decomposed and dissolved by
boiling nitric acid and also by boiling dilute sulphuric acid.

Separation
of CdS
from CuS. The latter reaction may be used to separate cadmium sulphide
from copper sulphide. Cadmium sulphide cannot be precipi-
tated from a solution which contains much hydrochloric acid.

**157.** Ammonia precipitates from cadmium solutions white
$Cd(OH)_2$. cadmium hydrate, which easily dissolves in an excess of
ammonia.

## GROUP VI.

### TIN, ARSENIC, ANTIMONY, (GOLD, PLATINUM).

**158.** Metals of this group are precipitated, as sulphides,
from acid solutions of their salts by hydrogen sulphide; and
their sulphides are soluble in ammonium sulphide.[1]

Oxides of
metals of
Group VI. Their lower oxides ($SnO$, $As_2O_3$[2], $Sb_2O_3$) act as bases,
while their higher oxides ($SnO_2$, $As_2O_5$, $Sb_2O_5$) exhibit the
deportment of anhydrides, that is, in combination with water
they form acids, with bases, salts.

#### TIN, Sn II and IV.

**159.** Tin is a malleable, silvery white metal, which does
not tarnish and which is but little attacked by dilute sulphuric
acid. It dissolves readily in warm, concentrated hydrochloric

General
properties
of tin. acid, with difficulty in the diluted acid, to form a colorless
solution of stannous chloride. Concentrated nitric acid con-
verts it, with the evolution of brown fumes, into insoluble
metastannic acid, $H_2SnO_3$. It dissolves in cold, dilute, nitric
acid, as stannous nitrate, $Sn(NO_3)_2$.

Stannous salts are converted into stannic salts by *aqua regia*
and by other oxidizing agents. In the oxidizing flame, tin is very
easily oxidized to stannic anhydride, $SnO_2$, a yellowish white

---

[1] The ammonium sulphide referred to here is a solution of the salt which has
become yellow by keeping, or by the addition of sulphur, and which, therefore,
contains some ammonium poly-sulphide, such as $(NH_4)_2S_2$ or $(NH_4)_2S_3$, etc.

[2] This oxide acts both as an anhydride and as a base.

powder, which is infusible and non-volatile, and which becomes greenish blue when moistened with cobaltous nitrate and then strongly ignited.

**160.** Acid solutions of stannous salts give with hydrogen sulphide a brown precipitate, consisting of a compound of stannous sulphide, SnS, with water. This precipitate becomes black when dried. The addition of hydrogen sulphide to an acid stannic solution produces a yellow precipitate, consisting of a mixture of stannic sulphide, $SnS_2$, and stannic anhydride, $SnO_2$. *SnS.*

Both of these precipitates dissolve in yellow ammonium sulphide. If either of the solutions so obtained be acidified with hydrochloric acid, the tin is precipitated as yellow stannic sulphide, $SnS_2$. *SnS₂.*

**161.** The tin may be entirely precipitated from either a stannous or stannic solution as metastannic acid, $H_2SnO_3$, by prolonged boiling with an excess of nitric acid. *Precipitation of $H_2SnO_3$.*

**162.** Solutions of stannous salts have a powerful reducing action. They will therefore decolorize starch paste, which has been made blue by the addition of a little iodine solution; they will change the red color of a mixture of potassium pyrochromate and sulphuric acid to a green (§222); they will turn blue a mixture of ferric sulphate and potassium ferricyanide (§96); they will precipitate mercurous chloride from a solution of mercuric chloride (§125). The last mentioned of these reactions is the most generally applicable and characteristic. *Reducing action of stannous compounds.*

**163.** If a solution of a stannic salt is neutralized with ammonia, potassium hydrate, sodium hydrate, or with a carbonate, a gelatinous precipitate of stannic acid, $H_2SnO_3$, is formed, which is readily soluble, in acids to form stannic salts, in alkalies to form stannates. *Stannic acid.*

$$H_2SnO_3 + 4HCl = SnCl_4 + 3H_2O$$
$$H_2SnO_3 + 2NaOH = Na_2SnO_3 + 2H_2O$$
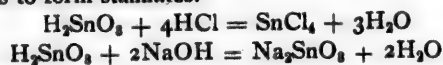
Under certain conditions, which are imperfectly understood, stannic acid changes into metastannic acid, which has the same composition, but is insoluble in acids.

**Reduction of Sn with Zn.**

**164.** If a fragment of zinc be introduced into an acidified stannic solution, the latter will be reduced, first to a stannous salt, and then to metallic tin, which will be deposited upon the zinc, in spongy form or in crystals. The deposit may be dissolved in a little strong hydrochloric acid and tested according to §162.

**Reduction of Sn with "Cyanide flux."**

**165.** All tin compounds can be reduced with sodium carbonate on charcoal (§12). This reduction is difficult and requires the prolonged action of a powerful reducing flame. If, instead of sodium carbonate, the tin compound be mixed with "cyanide flux" (v. note §12), the reduction to globules of metallic tin is more easily effected.

$$SnO_2 + 2KCN = 2KOCN + Sn$$

### ARSENIC, As III and V.

**Blowpipe reactions of arsenic.**
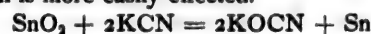
**166.** Arsenic is a brittle, grayish white element of metallic lustre. It is sometimes classified as a metal, sometimes as a non-metal. Most of its compounds are volatile, and all are poisonous. Heated on the charcoal stick with the blowpipe flame, it burns to arsenous oxide, $As_2O_3$, which appears as a white smoke and which is partly deposited as a volatile white film, at some distance from the assay piece, a characteristic odor resembling that of garlic, being given off at the same time. A fragment of arsenic, when heated in the closed tube or matrass, is sublimed and deposited as a shining metallic mirror in the colder part of the tube.

Arsenic is readily oxidized and dissolved by hot nitric acid or by hot, concentrated sulphuric acid.

**$As_2S_3$.**

**167.** Hydrogen sulphide produces, in acidified solutions of arsenous compounds, a canary-yellow, curdy precipitate of arsenous sulphide, $As_2S_3$, which is easily soluble in ammonium sulphide, and which is precipitated from this solution on acidification with hydrochloric acid.

**Arsenous distinguished from arsenic compounds.**

Arsenic solutions (*i. e.* those containing pentavalent arsenic) are precipitated in the same way by hydrogen sulphide, but, in this case, the precipitation is exceedingly slow, one or two days being required, since the *arsenic* compound must be

ES.                    [§167

uced into an acidified
ced, first to a stan-
ch will be deposited
rystals.  The deposit
chloric acid and tested

educed with sodium
duction is difficult and
erful reducing flame.

compound be mixed
reduction to globules

N + Sn

hite element of metal-
s a metal, sometimes
nds are volatile, and
arcoal stick with the
oxide, $As_2O_3$, which
partly deposited as a
om the assay piece, a
garlic, being given off
ic, when heated in the
deposited as a shining
tube.

lved by hot nitric acid

, in acidified solutions
w, curdy precipitate of
y soluble in ammonium
n this solution on acidi-

ng pentavalent arsenic)
drogen sulphide, but, in
ngly slow, one or two
ic compound must be

reduced to the *arsenous* condition, before precipitation can take place.

$$H_3AsO_4 + H_2S + 3HCl = AsCl_3 + 4H_2O + S$$
$$2AsCl_3 + 3H_2S = As_2S_3 + 6HCl$$
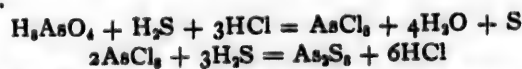
**168.** If an exactly neutral solution of an arsenous compound is treated with silver nitrate, a bright yellow precipitate of silver arsenite, $Ag_3AsO_3$, is formed, which dissolves easily in acids or alkalies.[1]  $Ag_3AsO_3$.

$$Na_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NaNO_3$$
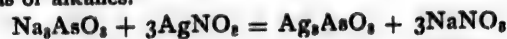
Since it is difficult to make an arsenous solution exactly neutral, it is well to proceed as follows.

Render the solution slightly acid with nitric acid and pour carefully upon it, without mixing, a solution of silver nitrate, previously made slightly alkaline with ammonia.  Between the two liquids there will be a neutral zone, in which the precipitate will appear as a yellow ring.

**169.** Boiling nitric acid converts arsenous compounds into arsenic acid.   Conversion of arsenous into arsenic compounds

$$As_2O_3 + 2HNO_3 = 2H_3AsO_4 + N_2O_3$$

Arsenic acid, when neutralized with ammonia and treated with silver nitrate, according to the method described in the foregoing paragraph, gives a brick-red precipitate of silver arsenate, $Ag_3AsO_4$; soluble in the mineral acids and in ammonia; nearly insoluble in dilute acetic acid.  For other reactions of arsenic acid, see §§215–218.

**170.** If a solution containing arsenic be warmed with a large excess of concentrated hydrochloric acid and a piece of tin foil, a brownish precipitate of finely divided metallic arsenic will appear.

**171.** If an arsenous solution be acidified with hydrochloric acid and the mixture digested for some time with a clean piece of copper foil, the latter will become covered with a shiny black coating of copper arsenide.  The coated copper should be thoroughly washed, dried, and heated in the open tube (§15).  Brilliant, microscopic crystals of $As_2O_3$ will form in   Reinsch's test for arsenic.

[1]Chlorides, bromides and iodides, which precipitate silver nitrate, interfere more or less with this test.

the upper part of the tube.[1] In case the coating on the copper should be small in quantity, it would be better to heat it in a closed, instead of an open tube, of hard glass, about three sixteenths of an inch in outside diameter. The reason for this is that the strong current of hot air through the open tube might well carry off and dissipate very small quantities of arsenic, an accident which can not happen in using a matrass.

**Marsh's test.**

**172.** If a very small quantity of a solution containing arsenic be added to a mixture of dilute sulphuric acid and zinc, the escaping hydrogen will contain arsine, $AsH_3$, which has a very characteristic odor. If the gas be passed through a hard glass tube, two or three inches of which are heated by a Bunsen flame, metallic arsenic will be deposited as a brilliant, brownish black mirror, beyond the heated part of the tube. (Compare §177.)

**Arsenical mirror and spots.**

If the gas, as it escapes from the end of the tube, is ignited, the flame will burn with a pale blue color, different from that of pure hydrogen, and will emit an odor resembling that of garlic. If a cold porcelain dish be held in the flame, a brilliant black spot of metallic arsenic will be deposited upon it.

**173.** When an arsenic compound is heated in the blow-pipe flame, on charcoal, the odor and film mentioned in §166 may be observed.

### ANTIMONY, Sb III & V.

**Properties of antimony.**

**174.** Antimony is a brittle, white metal of high metallic lustre. When heated on charcoal, in the oxidizing flame, it burns with a bluish flame, depositing a white coating of antimonous oxide, $Sb_2O_3$, on the charcoal. This film is less volatile and forms closer to the assay than the analogous incrustation of arsenous oxide. Antimony is very fusible, and much less volatile than arsenic. The metal is insoluble in hydrochloric or dilute sulphuric acids; dilute nitric acid oxidizes it to antimonous oxide, $Sb_2O_3$; hot concentrated nitric acid

---

[1] REMARK:—Under the conditions given, a solution containing *antimony* will produce a dull black stain on the copper, but no octahedral crystals can be obtained by subsequent heating in the tube, unless arsenic is present.

**Left margin fragments:**

ating on the copper
better to heat it in a
glass, about three
The reason for this
ough the open tube
small quantities of
n in using a matrass.
solution containing
sulphuric acid and
arsine, $AsH_3$, which
be passed through
which are heated by
eposited as a brilliant,
ted part of the tube.

of the tube, is ignited,
or, different from that
or resembling that of
n the flame, a brilliant
osited upon it.

heated in the blow-
lm mentioned in §166

metal of high metallic
the oxidizing flame, it
white coating of anti-
l.   This film is less
than the analogous
ny is very fusible, and
metal is insoluble in
dilute nitric acid oxid-
concentrated nitric acid

tion containing *antimony* will
o octahedral crystals can be
arsenic is present.

---

converts it into metantimonic acid, $H_3SbO_3$, a nearly insoluble compound; *aqua regia* dissolves it as antimonic chloride, $SbCl_3$.

**175.** Hydrogen sulphide precipitates antimonous sulphide, $Sb_2S_3$, from acid solutions of antimonous compounds, and the same precipitate, mixed with antimonic sulphide ($Sb_2S_5$), from similar solutions of antimonic compounds. The sulphides of antimony dissolve in yellow ammonium sulphide. When this solution is acidified with hydrochloric acid, the whole of the antimony is thrown down as an amorphous, orange precipitate of antimonic sulphide, $Sb_2S_5$. *(margin: $Sb_2S_3$. $Sb_2S_5$.)*

**176.** Neutral or slightly acid solutions of antimony readily become opalescent and deposit a precipitate, especially when boiled. In the case of antimonic compounds this precipitate consists of metantimonic acid, $HSbO_3$, in the case of antimonous compounds, it consists of a basic salt, for example, $SbOCl$, antimonyl chloride.[1] *(margin: Instability of antimony solutions.)*

**177.** An antimony solution, when treated as described in §172, forms a mirror or stains of metallic antimony, which differs from the arsenical mirror in being soot-black and without lustre, when deposited directly from the flame on a porcelain plate, but which often posess a silvery lustre when formed in a heated tube. In the latter case the mirror sometimes appears on both sides of the heated portion of the tube. The escaping gas, when burnt, gives no odor of garlic.

**178.** Alkaline solutions of antimonous compounds, which may be looked upon as solutions of salts of the hypothetical antimonous acid, $H_3SbO_3$, precipitate metallic silver from a solution of silver nitrate. The subsequent addition of ammonia redissolves any silver oxide, which may have been precipitated at the same time, leaving the reduced silver as a fine black powder. *(margin: Reduction of silver by $As_2O_3$.)*

The test can be applied, in a modified form, directly to the antimonous film obtained by heating antimony compounds on charcoal or in the open tube. If such a film be moistened with

---

[1] Analogous to bismuthyl chloride, $BiOCl$. Basic antimony compounds may be distinguished from those of bismuth by the fact that the former only are soluble in tartaric acid.

silver nitrate, and then be subjected to the action of the vapour of strong ammonia water, it will turn black, in consequence of a reduction of the silver salt.

Zinc
reduction
test.

**179.** If a piece of platinum foil be immersed in a solution of antimony acidified with hydrochloric acid, and a piece of zinc be placed in the liquid, in contact with the foil, a sooty stain of metallic antimony will be deposited upon the latter.

This reaction distinguishes antimony from the other metals of this group.

**180.** If an antimony compound, mixed with sodium carbonate and potassium cyanide, be exposed to the blowpipe reducing flame on charcoal, globules of metallic antimony will be produced, which can be recognized by the properties of the metal as given in §174, after separation from the flux by digestion with water.

### PLATINUM, Pt II to VI.

Proper-
ties of
platinum.

**181.** Platinum is a bluish white, malleable metal, infusible in the Bunsen flame; insoluble in nitric acid, hydrochloric acid, sulphuric acid; soluble (but slowly) in *aqua regia*, forming chloro-platinic acid, $H_2PtCl_6$, which has a deep orange-brown color and which, upon evaporation of its solution, is separated into hydrochloric acid and platinum chloride, $PtCl_4$.

Reduction.

**182.** The salts of platinum, when heated to redness, are decomposed with the separation of metallic platinum.

$PtCl_4$.

**183.** A solution of platinum in *aqua regia*, or chloro-platinic acid, when added to a solution of potassium chloride, throws down a yellow precipitate consisting of octahedral crystals of potassium chloro-platinate, $K_2PtCl_6$. In making this test, a drop of each of the solutions should be mixed upon a microscope slide.

$K_2PtCl_6$.

### GOLD, Au I & III.

Au.

**184.** Gold is a soft, malleable metal of characteristic color, insoluble in hydrochloric, nitric and sulphuric acids; but readily soluble in *aqua regia*, as auric chloride, $AuCl_3$.

. action of the vapour
k, in consequence of

amersed in a solution
acid, and a piece of
ith the foil, a sooty
ed upon the latter.
rom the other metals

ed with sodium car-
sed to the blowpipe
metallic antimony will
by the properties of
on from the flux by

alleable metal, infusi-
ric acid, hydrochloric
) in *aqua regia*, form-
has a deep orange-
tion of its solution, is
tinum chloride, $PtCl_4$.
heated to redness, are
llic platinum.

*qua regia*, or chloro-
of potassium chloride,
sisting of octahedral
$K_2PtCl_6$. In making
ions should be mixed

metal of characteristic
nd sulphuric acids; but
hloride, $AuCl_3$.

---

**185.** At a red heat, the salts of gold are decomposed, Reduction by heat. the gold being separated as a sponge, which, before the blow-pipe, can be fused to globules of metallic gold.

**186.** If a solution of ferrous sulphate, or of oxalic acid, in excess, be added to a solution of a gold salt, the gold is reduced to the metallic state and appears as a finely divided, dull brown precipitate, which, when dried and rubbed, exhibits metallic lustre. Reduction by $FeSO_4$.

**187.** If a gold solution is treated with a mixture of stan-nous and stannic chlorides, a purple coloration or precipitate appears. Purple of Cassius.

This reaction is most delicate. The precipitated substance is called *Purple of Cassius*, its chemical constitution being unknown.

# CHAPTER III.

## REACTIONS OF THE ACIDS.

**188.** The more commonly occurring acids are divided into five analytical groups, according to their behaviour toward the group-reagents, barium chloride, silver nitrate and potassium acetate. Some of these groups are further subdivided. The following section presents a general view of the classification.

### SYNOPSIS OF THE CLASSIFICATION OF THE ACIDS.

#### GROUP I.

$H_2SO_4$. SULPHATES.

**189.** Precipitated by barium chloride from solutions acidified with hydrochloric acid.

#### GROUP II.

Precipitated by barium chloride from neutral solutions, but not from those acidified with hydrochloric acid.

DIVISION 1. $H_2CO_3$, $H_2SO_3$, $H_2C_2O_4$, HF.
CARBONATES, SULPHITES, OXALATES, FLUORIDES.

Decomposed by concentrated sulphuric acid with the evolution of gas.

DIVISION 2. $H_2CrO_4$, $H_3PO_4$, $H_3AsO_4$, $H_3BO_3$, $H_2SiO_3$.
CHROMATES, PHOSPHATES, ARSENATES, BORATES, SILICATES.

Evolve no gas with concentrated sulpuric acid.

42

### GROUP III.

Precipitated by silver nitrate from dilute solutions acidified with nitric acid.

DIVISION 1.  HSCN, $H_4FeC_6N_6$, $H_3FeC_6N_6$.
SULPHOCYANATES, FERROCYANIDES, FERRICYANIDES.

Give a red or blue coloration with iron salts.

DIVISION 2.  HClO, $HClO_2$, $HNO_2$. $(Cl_2, Br_2, I_2)$.
HYPOCHLORITES, CHLORITES, NITRITES, (FREE HALOIDS.)

Bleach indigo solution.

DIVISION 3.  $H_2S_2O_3$, $H_2S$.
THIOSULPHATES, SULPHIDES, POLYSULPHIDES.

Give a black precipitate with silver nitrate, either at once or on boiling.

DIVISION 4.  HCl, HBr, HI, HCN.
CHLORIDES, BROMIDES, IODIDES, CYANIDES.

Do not give reactions of divisions 1, 2 and 3.

### GROUP IV.

$H_2C_4H_4O_6$, TARTRATES.

Precipitated by potassium acetate from solutions acidified with acetic acid.

### GROUP V.

$HOCOCH_3$, $HClO_3$, $HNO_3$.
ACETATES, CHLORATES, NITRATES.

Not precipitated by either of the group-reagents.

---

### GROUP I.

#### SULPHURIC ACID AND SULPHATES, $R_2SO_4$.

**190.** Free sulphuric acid, after concentration, will blacken cane sugar or paper if heated to 100°. If lines are drawn on writing paper with water containing a small quantity of free sulphuric acid, and the paper be then cautiously dried and heated, the lines will turn brown or black.

*Free $H_2SO_4$.*

BaCl₂
test.

**191.** Barium chloride produces, even in extremely dilute solutions of sulphuric acid or sulphates, a finely divided, white, crystalline precipitate of barium sulphate; nearly insoluble in dilute acids or alkalies; soluble in hot, concentrated sulphuric acid.

**192.** In applying the foregoing test for sulphuric acid, you must be careful not to have too much nitric or hydrochloric acid present, and to make the solution sufficiently dilute. If strong nitric acid be added to a solution of barium chloride, a white precipitate of barium nitrate appears, which might be mistaken for barium sulphate, and, similarly, strong hydrochloric acid will precipitate barium chloride from a solution of that salt; the reason for the precipitation being, in both cases, the fact that the salts named are much less soluble in strong nitric or hydrochloric acid than in pure water.

Reduction
test.

**193.** Any sulphate, when heated with sodium carbonate in the reducing flame, is reduced to sodium sulphide, which is absorbed by the charcoal. If the contiguous part of the charcoal be dug out with a pen-knife blade, placed on a silver coin and moistened, the silver will soon be blackened, from the formation of silver sulphide.[1]

$$Na_2S + Ag_2 + H_2O + O = Ag_2S + 2NaOH$$

### GROUP II.

#### DIVISION I.

#### SULPHITES, CARBONATES, OXALATES AND FLUORIDES.

**194.** This division includes those acids which are precipitated by barium chloride in neutral but not in hydrochloric acid solutions, and which evolve a gas when treated with concentrated sulphuric acid.

SULPHUROUS ACID, AND SULPHITES, $R_2SO_3$.

Free
$H_2SO_3$.

**195.** Free sulphurous acid is known only in solution. It has a strongly pungent odor and an acid reaction. It evolves

---

[1] Sulphites, thiosulphates and all other compounds of sulphur give the same reaction.

in extremely dilute
inely divided, white,
te; nearly insoluble
t, concentrated sul-

for sulphuric acid,
ch nitric or hydro-
solution sufficiently
a solution of barium
trate appears, which
nd, similarly, strong
chloride from a solu-
itation being, in both
much less soluble in
pure water.

th sodium carbonate
m sulphide, which is
ous part of the char-
laced on a silver coin
blackened, from the

g₂S + 2NaOH

S AND FLUORIDES.

ids which are precipi-
t not in hydrochloric
hen treated with con-

TES, R₂SO₃.

n only in solution. It
d reaction. It evolves

ds of sulphur give the same

$SO_2$, especially when warmed, and slowly absorbs oxygen from the air, forming sulphuric acid.

**196.** If a sulphite (as $Na_2SO_3$) be treated with sulphuric or hydrochloric acid, the suffocating odor of sulphurous acid will be evolved. If a strip of filter paper, previously moistened with a solution of potassium ferricyanide and ferric sulphate[1] be held in the escaping vapours, it will turn blue.[2] *"Blue paper" test.*

$$Fe_2(SO_4)_3 + H_2SO_3 + H_2O = 2FeSO_4 + 2H_2SO_4$$
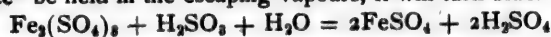
**197.** If sulphurous acid or a sulphite, be added to a highly dilute solution of iodine, the latter will be decolorized. The addition of a little fresh starch paste makes this test more delicate. *Iodine reaction.*

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$$

**198.** If sulphurous anhydride ($SO_2$) be conducted into bromine-water, it decolorizes the latter, forming sulphuric acid, which may then be detected by following §§190, 191. *Conversion into $H_2SO_4$.*

$$H_2SO_3 + Br_2 + H_2O = H_2SO_4 + 2HBr$$
$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$
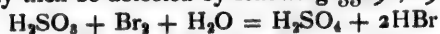
### CARBONIC ACID AND CARBONATES, $R_2CO_3$.

**199.** Free carbonic acid, $H_2CO_3$, is only known in solution. Its solution has a faintly acid reaction. When warmed, it evolves carbonic anhydride, $CO_2$, a nearly odorless, colorless gas, which may be recognized by its producing with lime water a white precipitate of calcium carbonate, $CaCO_3$. To perform this test, the gas may be passed into lime water; or a glass rod, with a drop of lime water suspended from it, may be held in the test tube above the surface of the liquid. It should be remembered that calcium carbonate is soluble in an excess of carbonic acid and that therefore the lime water must be present *in excess*. A solution of barium hydrate may be used with advantage instead of lime water, in which case there is nothing to be feared from an excess of carbonic anhydride, since it does not exert an appreciable solvent action on barium carbonate. *Free $H_2CO_3$.*

---

[1] This paper must be kept in the dark, if kept at all. It is best fresh (*v.* §96).
[2] Ferrous sulphate is formed, which produces Turnbull's blue with potassium ferricyanide (§92).

**200.** All carbonates are decomposed by dilute sulphuric (or hydrochloric or nitric) acid, carbonic acid, $H_2CO_3$, being set free. The latter may then be recognized by its characteristics as given in the preceding paragraph, especially by the reaction with calcium hydrate.

*Action of acids on carbonates.*

**201.** The only carbonates which are freely soluble in water are potassium carbonate, sodium carbonate and ammonium carbonate. These have an alkaline reaction. A precipitate is formed when a soluble carbonate is mixed with a neutral solution of a salt of any base[1] except sodium, potassium or ammonium.

*Solubility of carbonates.*

**202.** The bicarbonates or acid carbonates of sodium and potassium ($NaHCO_3$, $KHCO_3$) may be distinguished from the normal carbonates ($Na_2CO_3$, $K_2CO_3$) by the fact that the latter turn turmeric paper brown while the former do not (§23).

*Bicarbonates.*

### Oxalic Acid and Oxalates, $R_2C_2O_4$.

**203.** Free oxalic acid, $H_2C_2O_4 + 2H_2O$, is a white, crystalline, strongly acid solid, readily soluble in water. The free acid and its salts give no reaction with *dilute* sulphuric acid (difference from the carbonates), but, when warmed with *concentrated* sulphuric acid, an effervescence takes place, due to the escape of $CO$ and $CO_2$, the oxalic acid being decomposed according to the following equation:

*Oxalates.*

*Decomposition of.*

$$H_2C_2O_4 = H_2O + CO + CO_2.$$

**204.** Solutions of an oxalate give with calcium salts a precipitate of calcium oxalate, $CaC_2O_4$, even in very dilute neutral solutions. This precipitate is colorless, micro-crystalline, soluble in the mineral acids, insoluble in acetic acid (§46). It is easily converted by heat into calcium carbonate and carbon monoxide.

*Precipitation of, by calcium salts.*

**205.** Oxalic acid or an oxalate when boiled with a strongly acidified solution of potassium dichromate causes the

*Reaction with $H_2CrO_4$.*

---

[1] Some bases which also have acidic properties form exceptions, such as $As_2O_3$, etc.

color to change from red to green, in consequence of a reduction of chromic acid to a chromic salt. For example:

$$K_2Cr_2O_7 + 3H_2C_2O_4 + 4H_2SO_4 =$$
$$K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 6CO_2$$
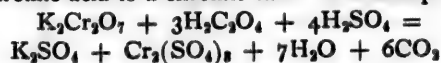
**206.** Soluble oxalates give precipitates with most metallic salts, copper sulphate, nickel sulphate, manganese sulphate, and many others.

### HYDROFLUORIC ACID AND FLUORIDES, RF.

**207.** Hydrofluoric acid is an exceedingly acid, volatile, corrosive liquid, which etches glass. In order to exhibit this property, warm a plate of glass and rub a lump of wax over **HF** it so as to give it a thin and even coating of wax. After **etches** cooling, write firmly on the surface with a pencil or any other **glass.** hard point. Then submit the surface to the action of hydrofluoric acid. It will be etched wherever the wax coating is scratched. Remove the wax by again warming the plate and wiping off the wax while warm. The writing will now be visible as an etching on the glass.

**208.** If a fluoride is treated with concentrated sulphuric acid, hydrofluoric acid is set free and may be recognized by **Test for** its pungent odor and other characteristics. Mix the substance **fluorides.** to be tested (which should be dry) with concentrated sulphuric acid in a shallow leaden dish. Cover the dish immediately with a glass plate, prepared as described in the preceding paragraph, the waxed surface downward, and allow the whole to stand over night. If the glass is etched, a fluoride is indicated.[1]

**209.** When only a small amount of substance is available, it may be advantageously tested for fluorides, as follows:

Pulverize it finely and dry it thoroughly, if not dry already. **Matrass** Mix with twice its bulk of acid potassium sulphate, $KHSO_4$, **test for** and introduce the mixture into a clean and dry matrass (§14). **fluorides.** Wipe out the upper part of the tube with filter paper. Heat

---

[1]This, and all other experiments with hydrofluoric acid, should be performed under the hood, and every precaution should be observed to avoid inhaling the acid vapour.

the mixture to calm fusion.  Cut off the tube at a point just
above the mixture.  Rinse out the upper part of the tube
with distilled water and dry it.  If etched, hydrofluoric acid is
indicated.  If the fluoride tested be fluor-spar, the reaction is
given by the equation:

$$CaF_2 + 2KHSO_4 = K_2SO_4 + CaSO_4 + 2HF$$

## DIVISION II.

### PHOSPHATES, ARSENATES, CHROMATES, BORATES AND SILICATES.

**210.**  This division includes those acids which are precip-
itated by barium chloride in neutral but not in acid solutions
and which evolve no gas when treated with concentrated
sulphuric acid.

The acids of this section are not readily volatile.

### ORTHOPHOSPHORIC ACID AND PHOSPHATES, $R_3HPO_4$ OR $R_3PO_4$.

**211.**  Free phosphoric acid, $H_3PO_4$, is a colorless, intensely
sour, oily liquid, which the application of heat converts into
metaphosphoric acid, $HPO_3$, a viscous, semi-solid mass.

$H_3PO_4$.

Free phosphoric acid and phosphates, when mixed with
ammonium chloride, ammonia to alkaline reaction and then
with magnesium chloride or sulphate, give a colorless, crystal-
line precipitate (§61), of ammonium magnesium phosphate,
$MgNH_4PO_4$; slightly soluble in water; insoluble in strong
ammonia-water; readily soluble in dilute acids.

Magnesia
mixture
test.

This precipitate, if filtered and washed, and then moistened
with silver nitrate, turns canary-yellow, from the formation of
silver phosphate.

$$MgNH_4PO_4 + 3AgNO_3 = NH_4NO_3 + Mg(NO_3)_2 + Ag_3PO_4$$

**212.**  Phosphates, when added to a nitric acid solution of
ammonium molybdate, give, either at once or on standing, a
yellow, granular precipitate of ammonium phospho-molybdate.
This is the most sensitive of the reactions for the detection of
orthophosphoric acid.  *Arsenic and silicic acids give similar
precipitates under similar conditions.*

Molybdate
test.

**213.**  Solutions of orthophosphates, when exactly neutral- Silver ized with ammonia and treated with silver nitrate, give a phosphate. yellow precipitate of silver phosphate, $Ag_3PO_4$, which is easily decomposed by dilute acids or alkalies.

**214.**  A neutral solution of an orthophosphate, when treated with neutral solutions of ferric or aluminium salts, gives a white precipitate (§100) of ferric phosphate, $FePO_4$, or $FePO_4$ aluminium phosphate, $AlPO_4$; insoluble in acetic acid, but $AlPO_4$. and soluble in the mineral acids.

If either of these precipitates be dried at a high temperature and then mixed with a little powdered metallic magnesium and strongly ignited in a matrass, magnesium phosphide will be formed, $Mg_3P_2$.

$$2FePO_4 + 11Mg = 2Fe + 8MgO + Mg_3P_2$$

If the residue be then moistened with a drop of hydrochloric acid, phosphine, $PH_3$, will be evolved and may be detected by its peculiar odor and by its property of emitting light in a darkened room.

ARSENIC ACID AND ARSENATES, $R_2HAsO_4$ OR $R_3AsO_4$.

**215.**  Free arsenic acid closely resembles free phosphoric Free acid, and its salts give reactions similar to those described in $H_3AsO_4$. §§211–212.  The precipitate of magnesium ammonium arsenate, $MgNH_4AsO_4$, is indistinguishable in appearance from magnesium ammonium phosphate, but may be distinguished from the latter by giving a red instead of a yellow coloration on treatment with silver nitrate.

$$MgNH_4AsO_4 + 3AgNO_3 =$$
$$Ag_3AsO_4 + NH_4NO_3 + Mg(NO_3)_2$$

**216.**  Solutions of an arsenate, when exactly neutralized with ammonia and treated with silver nitrate, give a brick-red $Ag_3AsO_4$. precipitate of silver arsenate, $Ag_3AsO_4$, soluble in dilute acids or alkalies.  Silver arsenate is much less soluble in acetic acid than silver phosphate.

**217.**  An arsenate, on gently warming with a large Tin test. excess of concentrated hydrochloric acid and tin foil, will give a brownish precipitate of finely divided arsenic.  (Distinction from all other acids of this group).

**218.** Other tests for arsenic acid are given under the head of arsenic, §§166–173.

### CHROMIC ACID AND CHROMATES, R₂CrO₄.

**219.** Chromic acid, $H_2CrO_4$, is not known in the free state, since it separates readily into $H_2O$ and $CrO_3$ (chromic

CrO₃. anhydride). The latter is a ruby-red, crystalline solid, readily soluble in water, to which it gives a reddish or yellowish coloration, even in highly dilute solutions. The soluble chromates give in neutral solutions with nitrate of silver a red

Ag₂CrO₄. precipitate of silver chromate, $Ag_2CrO_4$, soluble in ammonia and in mineral acids, nearly insoluble in acetic acid.

**220.** Mercurous nitrate gives a very similar reaction, precipitating the chromic acid as mercurous chromate, $Hg_2CrO_4$,

Hg₂CrO₄. blood-red.

**221.** Neutral solutions of chromates give, with barium chloride or nitrate, a yellow, and with lead nitrate or acetate, an orange-yellow precipitate, respectively $BaCrO_4$ (§55), and

BaCrO₄. $PbCrO_4$ (§134). Both these precipitates, especially the latter, are nearly insoluble in dilute acetic acid but are somewhat soluble in dilute mineral acids.

**222.** If a dilute solution of chromic acid, or of a chromate be acidified, treated with a few drops of alcohol and warmed,

Reduc- the color of the solution will change from red to green. Sul-
tion of phurous acid, hydrogen sulphide and many other reducing
CrO₃. agents will effect the same change.

$$2H_2CrO_4 + 3H_2SO_3 = Cr_2(SO_4)_3 + 5H_2O$$

### BORIC ACID AND BORATES.

**223.** Boric acid, $H_3BO_3$, is thrown down as a white,
H₃BO₃. crystalline precipitate on the addition of a strong acid to a concentrated solution of a borate.

**224.** Free boric acid, but not the borates, will impart a lively green coloration to the Bunsen flame. Borates, when moistened with sulphuric acid and introduced into the flame,

Flame give the same coloration which, however, is often masked by
test. the presence of sodium or some other flame-coloring base.

**225.** Alcohol, if boiled with free boric acid or with a mixture of sulphuric acid and a borate, gives off vapours,

re given under the

R₂CrO₄.

known in the free
and CrO₃ (chromic
stalline solid, readily
eddish or yellowish
.  The soluble chro-
rate of silver a red
soluble in ammonia
cetic acid.

similar reaction, pre-
chromate, Hg₂CrO₄

give, with barium
ad nitrate or acetate,
y BaCrO₄ (§55), and
, especially the latter,
d but are somewhat

acid, or of a chromate
alcohol and warmed,
n red to green.  Sul-
many other reducing

D₄)₃ + 5H₂O

s.

vn down as a white,
of a strong acid to a

borates, will impart a
llame.  Borates, when
duced into the flame,
r, is often masked by
lame-coloring base.

boric acid or with a
ate, gives off vapours,

which, when ignited, burn with a green flame.  No other *Alcohol*
substances will interfere with this test, which is most advanta- *test for*
geously executed as follows.  Provide a test-tube with a *H₃BO₃.*
closely fitting cork bearing a straight piece of glass tubing
about two inches long.  Introduce into the tube about 3 c.c.
of alcohol,[1] 1 c.c. concentrated sulphuric acid, and not too
small a quantity of the substance to be tested.

Warm the contents of the test tube gradually to boiling and
ignite the vapor as it issues from the delivery tube.  The
margin of the flame will appear green in the presence even
of a very small amount of a borate.

**226.**  If turmeric paper be immersed in a solution of a *Turmeric*
borate which has previously been acidified with hydrochloric *paper*
acid, the paper will turn red, either at once or upon drying. *test.*
The reddened turmeric blackens on treatment with ammonia.

**227.**  In neutral and somewhat concentrated solutions of
borates, barium chloride will produce a precipitate of varying
composition.  This test is neither sensitive nor characteristic.
Accordingly boric acid may often be detected by the test of
§225 in solutions which give no precipitate with barium
chloride.

### SILICIC ACID AND SILICATES.

**228.**  Free silicic acid, $H_2SiO_3$, has no acid reaction and *SiO₂.*
appears in, at least, three distinct forms: *a*, soluble in water,
*b*, gelatinous, *c*, insoluble in water, pulverulent.  The forms
*a* and *b* are converted into the insoluble form, *c*, if the solution
containing them is evaporated to dryness. *Separation*

A solution of any silicate, if it be acidified with hydrochloric *of SiO₂.*
acid, evaporated to dryness, and then treated with dilute
hydrochloric acid, will leave an insoluble residue of silicic
acid.  The solution will contain the bases (as chlorides) and
any other acids that were present.

**229.**  The only soluble silicates are those of sodium and *Insolu-*
potassium.  A solution of either of these may be precipitated *bility of*
by a salt of any other base. *silicates.*

[1] Methyl alcohol or wood spirit is preferable to common alcohol for the
purposes of this test.

**230.** Many silicates are incapable of being dissolved or decomposed by sulphuric or other strong acids. Such silicates may be fused with four times their weight of sodium carbonate and a little sodium nitrate. The product resulting from this fusion can be decomposed by boiling with dilute hydrochloric acid and water, and the silicic acid separated as in §228. The resulting solution can be used for the detection of other acids.

*Fusion of silicates.*

**231.** Silicic acid is soluble in aqueous hydrofluoric acid, forming fluosilicic acid, $H_2SiF_6$. If the latter is warmed with concentrated sulphuric acid, the whole of the silicon escapes in the form of the gas $SiF_4$. By further heating, the excess of hydrofluoric acid may also be expelled. In this way the silica may be removed from any silicate, the bases being at the same time obtained as sulphates.

*Expulsion of $SiO_2$.*

**232.** If silica or a silicate is fused with a bead of "microcosmic salt" (*v.* §11) in the oxidizing flame, the silica will remain floating as a cloud in the bead, and will render it opaque or opalescent when cold. Small quantities of silica can not always be detected by this test.

*Metaphosphate bead test.*

**233.** Silicic acid, $H_2SiO_3$, or silicic anhydride, $SiO_2$, into which the former is converted by ignition, dissolves in the sodium carbonate bead, forming a clear glass of sodium silicate, $Na_2SiO_3$.

If this bead be dissolved in dilute hydrochloric acid, the solution will *gelatinize*, either at once or on evaporation.

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$$
$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$

### GROUP III.

This group includes those acids which are precipitated by silver nitrate in a solution acidified by dilute nitric acid.

#### DIVISION I.

#### SULPHOCYANATES, FERROCYANIDES AND FERRICYANIDES.

**234.** This division comprises those acids which give a red or blue coloration with iron salts.

being dissolved or
acids.  Such silicates
of sodium carbonate
resulting from this
dilute hydrochloric
ted as in §228.  The
ection of other acids.
us hydrofluoric acid,
tter is warmed with
the silicon escapes in
eating, the excess of
In this way the silica
es being at the same

th a bead of " micro-
flame, the silica will
d, and will render it
ll quantities of silica

anhydride, $SiO_2$, into
tion, dissolves in the
ar glass of sodium

ydrochloric acid, the
on evaporation.

$_3 + CO_2$
$+ H_2SiO_3$

h are precipitated by
ilute nitric acid.

ANIDES AND

acids which give a red

## SULPHOCYANIC ACID AND SULPHOCYANATES, RSCN.

**235.**  Sulphocyanic acid is, in the free state, an oily, sour liquid, which readily decomposes.  It forms with the alkalies and alkaline earths colorless salts, which, when mixed with a *Ferric* ferric salt, give rise to an intense blood-red coloration, due to *sulpho-* the formation of a double ferric sulphocyanate.  For example: *cyanate.*

$$FeCl_3 + 12KSCN = 3KCl + Fe(SCN)_3(KSCN)_9$$

If this red solution be shaken with ether, the ethereal layer will acquire a deep red color.  This reaction is very sensitive and is peculiar to sulphocyanates.

**236.**  If a soluble sulphocyanate be treated with sulphurous *Cuprous* acid and copper sulphate, a white, amorphous precipitate of *sulpho-* $Cu_2(SCN)_2$, insoluble in dilute acids, will appear.  *cyanate.*

$$2CuSO_4 + 2KSCN + H_2SO_3 + H_2O =$$
$$Cu_2(SCN)_2 + 4K_2SO_4 + 2H_2SO_4$$
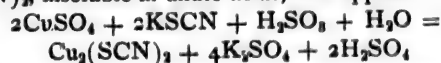
## HYDROFERROCYANIC ACID AND FERROCYANIDES, $R_4Fe(CN)_6$.

**237.**  Free hydroferrocyanic acid, $H_4Fe(CN)_6$, appears as a crystalline precipitate, consisting of colorless, pearly scales, difficultly soluble in water, when hydrochloric acid is added to a concentrated solution of a ferrocyanide.  The free acid readily decomposes, turning blue at the same time.

**238.**  The soluble ferrocyanides possess a pale yellow color.  They give with ferrous salts a colorless precipitate, which rapidly turns blue, with ferric salts a deep blue coloration or precipitate of Prussian blue.  The composition of these precipitates varies with the conditions of the experiment.

**239.**  Soluble ferrocyanides produce with copper salts, even in highly dilute solutions, a red precipitate, insoluble in the cold, in all acids.  This precipitate has the composition *Copper fer-* $Cu_2Fe(CN)_6$, when formed in the presence of an excess of *rocyanide.* copper salt.  If the ferrocyanide is in excess, the precipitate has the composition $Cu_3R_2(Fe(CN)_6)_2$.

$$2CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 2K_2SO_4$$
$$3CuSO_4 + 2K_4Fe(CN)_6 = Cu_3K_2(Fe(CN)_6)_2 + 3K_2SO_4$$
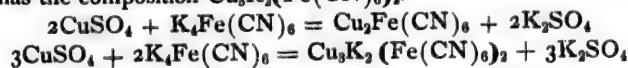
## HYDROFERRICYANIC ACID AND FERRICYANIDES, $R_3Fe(CN)_6$.

**240.**  Free hydroferricyanic acid is a soluble, reddish brown, crystalline substance.  The soluble ferricyanides are red salts,

the solutions of which are reddish yellow, even when highly dilute. With ferrous salts, they give a deep blue precipitate of Turnbull's blue, $Fe_3(CN)_{12}$. With ferric salts the ferricyanides give a deep reddish brown coloration but no precipitate.

**241.** If a soluble ferricyanide is slightly acidified with *Oxidising* hydrochloric acid and treated with zinc sulphate[1] and potas- *action of* sium iodide, the solution will turn brown, from the separation *ferricyan-* of iodine, and, if the solution be then shaken with chloroform, *ides.* the latter will turn violet; see §258.

$$K_6Fe(CN)_6 + KI = K_4Fe(CN)_6 + I$$
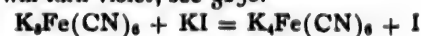
### DIVISION II.
### NITRITES, HYPOCHLORITES AND CHLORITES.

This division comprises those acids which bleach indigo solution.

#### NITROUS ACID AND NITRITES, RNO₂.

**242.** Free nitrous acid, $HNO_2$, spontaneously decomposes *Instability* into water and $N_2O_3$, and the latter into NO and $NO_2$, exhib- *of nitrous* iting the brown fumes or coloration of the latter. Nitrous *acid.* acid is set free from soluble nitrites when the latter are treated with hydrochloric or dilute sulphuric acid.

$$H_2SO_4 + 2NaNO_2 = Na_2SO_4 + 2HNO_2 =$$
$$Na_2SO_4 + H_2O + NO + NO_2$$
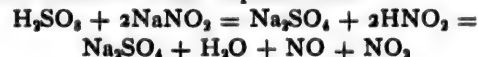
**243.** If a solution of a nitrite be colored blue with a drop of indigo solution, then acidified with acetic or hydrochloric acid and boiled, the blue color of the indigo will be destroyed.

Nitrates when treated with acetic acid and indigo solution do not destroy the color of the latter. This test may therefore be used to distinguished nitrites from nitrates.

**244.** A solution of a nitrite if treated with potassium iodide and then acidified, sets iodine free, and the latter may *Iodine test.* be detected by the blue color which it gives with starch paste (§259).

$$2NaNO_2 + 2KI + 4HCl = 2KCl + 2NaCl + N_2O_2 + 2H_2O + I_2$$

---

[1] The addition of the zinc sulphate, as recommended, greatly enhances the sensitiveness of this reaction.

**245.** The most delicate reaction for nitrites, known as Zambelli's test, may be executed as follows. Add to the solution sulphanilic acid, $NH_2C_6H_4SO_2H$, and acidify with dilute sulphuric acid. After standing a few minutes, add a drop of a saturated solution of phenol, $C_6H_5OH$, then render the solution alkaline with sodium hydrate. A yellow coloration indicates a nitrite. This extraordinarily sensitive reaction is more particularly adopted to the detection of nitrites in drinking water (§374).

*Zambelli's reaction.*

### Hypochlorous Acid and Hypochlorites, RClO.

**246.** Free hypochlorous acid has the peculiar and distinctive odor of chloride of lime. It decomposes very readily into hydrochloric acid, oxygen, and other products. Either the free acid or its salts, if mixed with a highly dilute indigo solution, rapidly bleach the latter.

*Acidified hypochlorites liberate chlorine.*

**247.** A hypochlorite on treatment with hydrochloric acid evolves chlorine (§§252–254).

$$2NaOCl + 2HCl = 2NaCl + H_2O + Cl_2$$
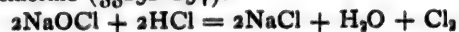
**248.** A hypochlorite when mixed with a drop of potassium iodide and acidified with hydrochloric acid sets iodine free.

### Chlorous Acid and Chlorites, RClO2.

**249.** Free chlorous acid is a very unstable compound resembling hypochlorous acid. Like the latter, it will bleach indigo solution. Chlorites, unlike the hypochlorites, will not bleach neutral or alkaline indigo solution, but will do so if acidified with hydrochloric or sulphuric acid.

**250.** Chlorites give reactions similar to those of the hypochlorites mentioned in §§247–248.

### Free Haloids, Cl2, Br2, I2.

**251.** The free haloids, chlorine, bromine and iodine, may be properly considered here, since, although not acids, they form a precipitate with silver nitrate in neutral or acid solutions and bleach indigo.

**252.** Free chlorine is a yellow gas, which dissolves in water to form a yellow solution possessing the suffocating

Reactions of free chlorine. odor of the gas. Chlorine-water, when treated with ammonia, causes an effervescence of nitrogen and simultaneous formation of ammonium chloride.

$$3Cl_2 + 8NH_3 = N_2 = 6NH_4Cl$$

**253.** If potassium bromide be added in excess to chlorine-water and the whole shaken with chloroform, the latter will turn brown (§255).

$$KBr + Cl = KCl + Br$$

If treated in a similar way with an excess of potassium iodide and chloroform, the latter will turn violet (§258).

$$KI + Cl = KCl + I$$

**254.** If a few drops of chloroform be colored faintly violet by the addition of a minute trace of iodine, and if it then be shaken with *an excess* of chlorine-water, the violet color will disappear in consequence of the formation of iodine trichloride.

$$I_2 + 3Cl_2 = 2ICl_3$$

Reactions of free bromine. **255.** Free bromine dissolves in water to the extent of about three *per cent.*, forming a reddish brown liquid, which smells of bromine, and which sets nitrogen free from ammonia.

$$3Br_2 + 8NH_3 = N_2 + 6NH_4Br$$
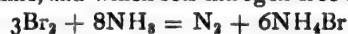
Bromine-water, if shaken with a few drops of chloroform or carbon disulphide, imparts to the latter a yellowish brown color, in consequence of a tendency which bromine exhibits, to leave the water, in which it is but slightly soluble, and to dissolve in the chloroform or carbon disulphide, in which it is freely soluble.

**256.** Bromine-water, when shaken with raw starch, colors the latter yellow.

**257.** Bromine if treated with potassium iodide in excess, liberates iodine.

Detection of free iodine. **258.** Iodine is but very slightly soluble in water, the solution being of a pale straw-color. It is much more freely soluble in a solution of potassium iodide in water. If either of these solutions is shaken with chloroform, the latter becomes violet.[1]

---

[1] The violet color is not due to a compound of iodine, since no chemical reaction occurs, but merely to a solution of iodine in chloroform.

By repeatedly shaking with fresh portions of chloroform the whole of the free iodine may be removed.

**259.** If to a dilute starch paste, prepared by boiling one gram of starch with 100 c.c. water for five minutes, be added a dilute iodine solution, the starch paste will acquire a beautiful blue color. This is the most sensitive and characteristic reaction for free iodine. The reaction does not take place in hot solutions. The starch paste should be used fresh. It may however be preserved for some weeks by keeping it in a tightly stoppered bottle containing a drop of chloroform.

*[margin: Starch paste reaction.]*

### DIVISION III.

### SULPHIDES, POLYSULPHIDES AND THIOSULPHATES.

**260.** This division comprises those acids which give a *black* precipitate with acid solutions of silver nitrate.

#### SULPHIDES, R$_2$S, AND POLYSULPHIDES, R$_2$S$_x$.

**261.** Hydrogen sulphide is a colorless gas, having a characteristic odor, which gives a black precipitate with alkaline, neutral or acid solutions of silver or lead.

A test paper, prepared by soaking white paper in a solution of nitrate of lead and then drying it, offers a convenient means of detecting this compound. A strip of it is rapidly browned or blackened, when brought into contact with hydrogen sulphide.

*[margin: Lead paper as a test for sulphides.]*

A solution containing sufficient free iodine to be of a straw-color is instantly decolorized by hydrogen sulphide.

$$H_2S + I_2 = 2HI + S$$

**262.** A soluble, normal, metallic sulphide, R$_2$S, if acidified with dilute sulphuric acid, evolves hydrogen sulphide (which may be recognized as above) without separation of sulphur.

$$K_2S + H_2SO_4 = K_2SO_4 + H_2S$$

**263.** A soluble, normal, metallic sulphide, if moistened and placed in contact with a clean piece of metallic silver, produces a black stain upon the latter.

$$Na_2S + Ag_2 + O + H_2O = Ag_2S + 2NaOH$$

**264.** A soluble, metallic polysulphide (usually yellow), when acidified with dilute hydrochloric or sulphuric acid, evolves hydrogen sulphide, free sulphur appearing at the

*[margin: Polysulphides.]*

same time as a white precipitate. This separation of free sulphur distinguishes the polysulphides from the normal sulphides.

$$H_2S_x + 2HCl = 2KCl + H_2S + S_{x-1}$$

### THIOSULPHATES, $R_2S_2O_3$.

**265.** Free thiosulphuric acid, $H_2S_2O_3$, rapidly decomposes, when in concentrated solution, into sulphurous acid, $H_2SO_3$, and free sulphur, each of which may be recognized by the appropriate tests (§196, 198). Highly dilute solutions decompose in the same way but much more slowly.

**266.** If a dilute solution of a thiosulphate is acidified, thiosulphuric acid is set free. The latter then decomposes as given above, the solution slowly turning milky from the separation of free sulphur.

*Reaction of thiosulphates with silver nitrate.* **267.** A solution of a thiosulphate, $R_2S_2O_3$, gives with silver nitrate a whitish yellow precipitate of silver thiosulphate, $Ag_2S_2O_3$. This compound is insoluble in dilute acids, but soluble in a solution of a thiosulphate. It decomposes readily and on boiling turns black, from the formation of silver sulphide.

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$$
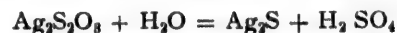
**268.** A solution of a thiosulphate instantly decolorizes an iodine solution.

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI$$

### DIVISION IV.

### CHLORIDES, BROMIDES, IODIDES AND CYANIDES.

**269.** This division comprises those acids which do not exhibit the reactions of Divisions I, II and III.

### HYDROCHLORIC ACID AND CHLORIDES, RCl.

*Test for chlorides with $AgNO_3$.* **270.** Free hydrochloric acid dissolves in water, forming a strongly acid solution. The free acid and its salts give with silver nitrate in neutral or acid solutions a curdy, white precipitate of silver chloride, $Ag_2Cl_2$, (*v.* note p. 27), which becomes violet on exposure to the light, especially in the presence of silver nitrate. The separation of this precipitate is greatly facilitated by violent shaking.
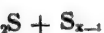
Silver chloride dissolves readily in ammonia or in a solution **Silver chloride.** of sodium thiosulphate. It is nearly insoluble in nitric acid.

**271.** If hydrochloric acid or a soluble chloride is treated with manganese dioxide and warmed with concentrated sulphuric acid, chlorine is liberated. (Cf. §§252–254.)

**272.** If a soluble chloride is warmed with a mixture of potassium dichromate and concentrated sulphuric acid, chromyl **Chromyl chloride.** chloride, $CrO_2Cl_2$, is formed. The latter is a volatile, red liquid, which, on warming, passes off as a red vapour. If the operation is performed in a tubulated test-tube, the vapour may be passed into ammonia to which it imparts a canary-yellow coloring owing to the formation of ammonium chromate.

$$K_2Cr_2O_7 + H_2SO_4 + 4HCl = K_2SO_4 + 2CrO_2Cl_2 + 3H_2O$$

$$CrO_2Cl_2 + 4NH_3 + 2H_2O = (NH_4)_2CrO_4 + 2NH_4Cl$$
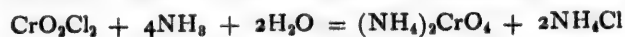
#### HYDROBROMIC ACID AND BROMIDES, R Br.

**273.** Hydrobromic acid, HBr, gradually turns brown when exposed to the air, in consequence of partial oxidation.

$$2HBr + O = H_2O + Br_2$$

The free acid or soluble bromides give with nitrate of silver **Silver bromide.** in neutral or acid solutions a curdy, yellowish precipitate of silver bromide. This is difficultly soluble in dilute ammonia; soluble in sodium thiosulphate; insoluble in acids.

**274.** Free hydrobromic acid or a soluble bromide, when treated cautiously with chlorine-water, drop by drop, turns brown, from the separation of free bromine.

$$HBr + Cl = HCl + Br$$
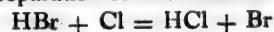
If the solution be then shaken with chloroform or carbon disulphide, this will be colored brown by the bromine.

**275.** Hydrobromic acid or soluble bromides, if warmed with concentrated sulphuric acid, or, better, with a mixture of sulphuric acid and manganese dioxide, evolve brown vapours of bromine.

#### HYDRIODIC ACID AND IODIDES, R I.

**276.** Solutions of free hydriodic acid rapidly turn brown in contact with the air, in consequence of oxidation.

Silver Iodide.

Hydriodic acid and soluble iodides give with silver nitrate a greenish yellow precipitate of silver iodide; insoluble in ammonia and in dilute acids; soluble in sodium thiosulphate solution. This precipitate does not readily darken on exposure to the light.

**277.** Hydriodic acid or a soluble iodide, when treated with chlorine-water or bromine-water, turns brown from the separation of free iodine.

$$HI + Cl = HCl + I$$
$$HI + Br = HBr + I$$

Reaction of I with starch.

The iodine set free in this reaction may be identified either by the addition of a few drops of dilute starch paste, with which it gives a blue coloration, or by shaking with chloroform in which it dissolves with a violet color.

An excess of the chlorine or bromine alters the reaction, iodine bromide or chloride being formed, instead of free iodine. (Compare equation §254.)

$$HI + 2Cl = HCl + ICl$$

Ferric salts with iodides.

**278.** A soluble iodide, when treated with a ferric salt, liberates iodine, which may be recognized as above.

$$Fe_2(SO_4)_3 + 2KI = K_2SO_4 + 2FeSO_4 + I_2$$

By boiling the mixture, the whole of the iodine may be expelled with the steam.

**279.** Any oxidizing agent, when added to an acidified solution of an iodide, sets the iodine free. Among the many oxidizing agents suitable for this purpose may be mentioned $K_2Cr_2O_7$, $KMnO_4$, $MnO_2$, $NaNO_2$.

Reaction with concentrated $H_2SO_4$.

**280.** A solution of an iodide is oxidized by warming with concentrated sulphuric acid, the iodine being set free.

$$2KI + 2H_2SO_4 = K_2SO_4 + H_2SO_3 + I_2 =$$
$$K_2SO_4 + I_2 + H_2O + SO_2$$

or $$6KI + 4H_2SO_4 = 3K_2SO_4 + 3I_2 + S + 4H_2O$$
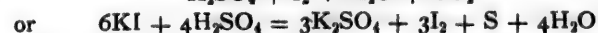
Concentrated nitric acid also liberates iodine from iodides.

**281.** A somewhat concentrated solution of a soluble iodide gives with lead nitrate a characteristic, beautiful yellow, crystalline precipitate of lead iodide, $PbI_2$. This reaction is characteristic, but not very delicate. Sulphates interfere with it.

with silver nitrate a
iodide; insoluble in
sodium thiosulphate
ly darken on expos-

iodide, when treated
rns brown from the

I
I
y be identified either
te starch paste, with
shaking with chloro-
olor.
e alters the reaction,
ned, instead of free

ICl
ed with a ferric salt,
ed as above.
2FeSO₄ + I₂
of the iodine may be

added to an acidified
e.  Among the many
ose may be mentioned

dized by warming with
being set free.
H₂SO₃ + I₂ =
SO₂

3I₂ + S + 4H₂O
iodine from iodides.
solution of a soluble
eristic, beautiful yellow,
PbI₂.  This reaction is
Sulphates interfere

### HYDROCYANIC ACID AND CYANIDES, RCN.

**282.**  Free hydrocyanic acid, HCN, is a feebly acid and very volatile liquid, the solutions of which readily undergo HCN. decomposition.  The free acid and simple cyanides are deadly poisons and must be handled with care.  A soluble simple cyanide, if treated with a ferrous salt, then rendered alkaline and boiled, forms a ferrocyanide.  The latter, on acidification with hydrochloric acid and treatment with a ferric salt, gives Prussian blue (*v.* §238).

$$6KCN + FeSO_4 = K_2SO_4 + K_4Fe(CN)_6$$

**283.**  The simple cyanides give upon the addition of silver nitrate in nitric acid solution a curdy, white precipitate Silver of silver cyanide, $Ag_2(CN)_2$.  This precipitate does not turn cyanide. dark on exposure to the light (in contra-distinction to silver chloride).  It is soluble in ammonia and in an excess of potassium cyanide.  It may be dissolved and decomposed by prolonged boiling with concentrated nitric acid.

**284.**  A simple cyanide is converted into a sulphocyanate by fusion with sulphur, or if its solution is boiled with yellow ammonium sulphide.  If after this treatment it is acidified with hydrochloric acid, then boiled and treated with ferric chloride, a blood-red color is produced.

### GROUP IV.

### TARTARIC ACID AND TARTRATES.

**285.**  Tartaric acid is a crystalline solid, very soluble in water.  It fuses at 135° and when heated to a higher temperature decomposes, giving off the odor of burnt sugar. Tartrates when heated give a similar odor.

**286.**  Tartaric acid prevents the precipitation of copper and ferric salts by potassium hydrate.  When a copper solution is mixed with tartaric acid and an excess of potassium hydrate, a deep blue solution is formed but no precipitate.

**287.**  If a solution of a tartrate is mixed with potassium "Cream acetate and then acidified with acetic acid, a crystalline pre- of tartar." cipitate of acid potassium tartrate, $KHC_4H_4O_6$, is thrown down (*v.* §34).

**288.** Neutral solutions of tartrates are precipitated by calcium chloride as calcium tartrate, $CaC_4H_4O_6 + 4H_2O$, or by barium chloride as $BaC_4H_4O_6 + H_2O$.

The calcium salt is much more insoluble than the barium salt. It dissolves in sodium or potassium hydrate and is somewhat soluble in the presence of ammonium salts.

## GROUP V.

**289.** Acids which give no precipitate with the group-reagents, barium chloride, silver nitrate, or potassium acetate.

### Acetates, Nitrates, Chlorates.

*Acetates.* **290.** The addition of sulphuric acid to an acetate sets free acetic acid, recognizable by its refreshing, sour odor. If concentrated sulphuric acid be added to three times its volume of alcohol, and the mixture gently warmed with an acetate, a peculiar fruity odor of ethyl acetate may be observed.

**291.** Acetates give, in concentrated solutions only, when treated with silver nitrate, a precipitate of silver acetate.

*Nitric acid.* **292.** Free nitric acid is a most powerful acid, which gradually turns yellow when exposed to the light.

$$2HNO_3 = H_2O + N_2O_4 + O$$

It has the property of turning many kinds of animal matter yellow, such as skin, finger nails, goose-quill, cooked albumen; a color which is deepened by the subsequent application of ammonia.

*"Xantho-proteic" reaction.* **293.** Nitric acid may be set free from a nitrate by the addition of concentrated sulphuric acid. If a nitrate be mixed with equal volumes of concentrated sulphuric acid and of water and then boiled with a quill tooth-pick, the latter will turn yellow. As a confirmatory test, it may be removed from the solution, washed and dipped in ammonia, when the color will change to an orange.

**294.** If a nitrate be mixed with a solution of ferrous sulphate and the mixture be poured carefully upon *concentrated* sulphuric acid in a test-tube, so as to form two layers, a violet-brown ring will appear at the juncture of the two liquids. This reaction is very delicate. (Compare §315.)

Iodides interfere with the reaction.  Should an iodide be originally present, it must first be removed by boiling the solution with ferric sulphate (§278).

**295.**  If a solution of a nitrate be mixed with its own volume of concentrated sulphuric acid and if, to the still hot mixture, a few drops of indigo solution be added, the blue color of the latter will rapidly change to yellow.  Acids of Division II, Group III, interfere with this reaction.

*Bleaching action of nitric acid.*

**296.**  If a dry nitrate be fused on charcoal, deflagration will ensue.

**297.**  Free chloric acid is a powerful acid, stable in dilute solutions, unstable in concentrated.  When treated with concentrated sulphuric acid a chlorate turns yellow, from the separation of chlorine tetraoxide, $Cl_2O_4$, etc.

$$2KClO_3 + H_2SO_4 = K_2SO_4 + H_2O + Cl_2O_4 + O$$

*Chlorates*
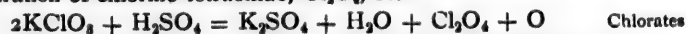
The $Cl_2O_4$ is evolved as a yellow gas, of penetrating odor, which explodes when touched with a hot wire and which rapidly bleaches a drop of indigo solution suspended in it on a glass rod.  It is dangerous to pour sulphuric acid upon potassium chlorate in any vessel larger than a test-tube.

**298.**  If a chlorate be treated with indigo and dilute sulphuric acid, the indigo will not be bleached, but if much concentrated acid be added, bleaching will occur.  This behaviour distinguishes the chlorates from the chlorites and hypochlorites (§§247–249).

If to the slightly acidified solution containing indigo and a chlorate, a small quantity of sodium sulphite be added, bleaching ensues; a characteristic reaction, dependent upon a reduction of the chlorate to a chlorite.

*Bleaching by chlorates.*

**299.**  A chlorate gives no precipitate with silver nitrate, but, if it is first fused on platinum foil, it will be converted into a chloride and the product when dissolved and treated with silver nitrate will give a precipitate of silver chloride.

*Conversion of chlorates into chlorides.*

**300.**  If a dry chlorate be fused on charcoal, deflagration will ensue.  If a dry chlorate be heated in a tube closed at one end, oxygen will be evolved, which may be detected by the aid of a glowing splinter.

# CHAPTER IV.

## SYSTEMATIC COURSE OF ANALYSIS FOR THE DETECTION OF ACIDS AND BASES.

### PRELIMINARY EXAMINATION.

**301.** The analysis of a solution, concerning the nature of which we have no clue, is naturally divided into three divisions: 1st, the preliminary examination; 2d, the detection of the acids; 3d, the detection of the bases. The object of the preliminary examination is to obtain, by means of a few tests, readily applied, some insight into the nature of the substance. The knowledge gained in this way often modifies and simplifies the analysis. So, for example, if we find in the preliminary examination that a solution contains sodium carbonate, we know at once that all those bases which are precipitated by alkaline carbonates must be absent, and that therefore, the labor of looking for them may be spared. To get the full benefit, which the preliminary examination may afford, requires the most thoughtful attention,[1] but it should on no account be be omitted or slighted. On the other hand, it should not be forgotten that only *indications* can be given, as a rule, by the preliminary examination and that often the reactions of different substances present will, more or less completely, alter or conceal one another.

In general, it is necessary to receive with caution the indica-

*Three chief steps in every analysis.*

---

[1]Table III shows which bases form soluble, and which insoluble, salts, with each acid, and it will be found a useful guide to the student in this connection.

IV.

LYSIS FOR THE
ND BASES.

ATION.

ncerning the nature of
vided into three divi-
; 2d, the detection of
s.  The object of the
means of a few tests,
ature of the substance.
n modifies and simpli-
find in the preliminary
sodium carbonate, we
ich are precipitated by
nd that therefore, the
ared.  To get the full
ion may afford, requires
hould on no account be
hand, it should not be
given, as a rule, by the
the reactions of differ-
less completely, alter or

with caution the indica-

nd which insoluble, salts, with
the student in this connection.

---

ions of the preliminary examination as to the presence or
bsence of certain bases or acids and to confirm the results by
applying further tests.

Should the substance to be analyzed not be already dis- Analysis
olved, directions for bringing it into solution will be found in of solids.
§348 and §379.

A portion of the material on hand for analysis should always
be set aside and reserved to guard against unforeseen accidents
and to use for special or confirmatory tests after the whole of
the regular course of analysis is gone over.

### FLAME TEST.

**302.** Dip a fine platinum wire[1] into the substance and
hold it in the hottest part of the flame of a Bunsen burner
(Fig. 1, *d;* p. 7), and observe the color of the flame.  If the
substance is a solid, it may be advantageous to moisten it with
hydrochloric acid previous to bringing it into the flame, for
the reason that the chlorides of some bases are more volatile
and impart a more pronounced color to the flame than the free
bases or their oxy-salts.

The following elements and their compounds afford, under
the given conditions, more or less characteristic indications.

| | | | |
|---|---|---|---|
| POTASSIUM: | The flame is violet, | . . . | §35 |
| BARIUM: | "  " green, | . . . | §51 |
| BORIC ACID: | "  " green, | . . . | §225 |
| COPPER: | "  " green, | . . . | §145 |
| PHOSPHORUS or PHOSPHITES: | "  " pale green. | | |
| SODIUM: | "  " bright yellow. | . . | §28 |
| CALCIUM: | "  " orange, | . . . | §43 |
| STRONTIUM: | "  " crimson, | . . . | §47 |
| LITHIUM: | "  " crimson. | | |
| ARSENIC (or ZINC): | "  " pale blue. | | |
| COPPER CHLORIDE: | "  " bright blue, | . . | §145 |
| ANTIMONY: | "  " greenish blue, | . | §174 |

---

[1] The platinum wire must first be so thoroughly cleaned that it will not color
the flame when held in it (*v.* §7, p. 7).

## EXAMINATION IN MATRASS AND OPEN TUBE.

**303.** This part of the preliminary examination is, of course, directly applicable only to solids. It is not usually worth while to evaporate a solution to dryness in order to test the behaviour of the residue in the matrass or in the open tube.

The closed tube is described in §14, where a list of the most characteristic reactions which may be observed by its aid may be found.

It should be made of very hard, difficultly fusible, thin glass, and it may be from three-sixteenths to three-tenths of an inch in external diameter, three to four inches being the most suitable length. For the indications of the open tube see §15.

## REDUCTION TEST.

Fusion on charcoal.

**304.** If the substance is a solution, this part of the preliminary examination, like the foregoing, is not directly applicable. If it is solid, moisten it with a drop of water and rub it up on a card to a stiff paste, using a pen-knife blade to incorporate the ingredients. Roll the mixture into the form of a pellet; place it in a hollow on the charcoal stick, and

Detection of sulphur.

fuse in the reducing flame for several minutes (§§12, 165). Dig out the mass, place it on a silver coin and moisten it. The formation of a black stain on the silver indicates sulphur, a sulphide, sulphite, sulphate, thiosulphate or a sulphocyanate. Carefully examine the fused mass for metallic globules or particles. To this end, it is sometimes well to rub it up in a mortar with a little hot water and then to allow a current of water from the wash-bottle to run through and over the residue. Under this treatment the powdered charcoal can be washed away, leaving the heavier metallic particles, if any, in

Separation of reduced metal.

the mortar. Under the pestle, globules of any malleable metal will be pressed into little disks or *laminæ*, whereas those of brittle metals, such as bismuth, will be broken into crystalline fragments. If a metal[1] has been reduced it may be:

---

[1] Consult Chapter II for suitable confirmatory tests for any of the metals enumerated. The metallic particles obtained may be examined by the blow-pipe according to the scheme laid down in Table I.

D OPEN TUBE.

y examination is, of
s. It is not usually
ryness in order to test
ss or in the open tube.
where a list of the most
served by its aid may

altly fusible, thin glass,
hree-tenths of an inch
s being the most suit-
open tube see §15.

r.

ion, this part of the
egoing, is not directly
th a drop of water and
g a pen-knife blade to
mixture into the form
the charcoal stick, and
l minutes (§§12, 165).
r coin and moisten it.
silver indicates sulphur,
ate or a sulphocyanate.
r metallic globules or
s well to rub it up in a
n to allow a current of
through and over the
vdered charcoal can be
allic particles, if any, in
of any malleable metal
*uinæ*, whereas those of
broken into crystalline
ced it may be:

---

tests for any of the metals
y be examined by the blow-
I.

| LEAD: | The globule is very soft. |
| ANTIMONY: | " " brittle, crystalline, white. |
| SILVER: | " " white, malleable. |
| BISMUTH: | " " gray, brittle. |
| COPPER: | " " red, malleable. |
| TIN: | " " white, malleable. |
| IRON: | The particles are gray, magnetic. |
| NICKEL: | The spangles are gray, magnetic, infusible. |
| COBALT: | " " " " magnetic, infusible. |

### SULPHURIC ACID TEST.

**305.** Acidify the substance, which may be either a solution or a solid, with dilute sulphuric acid. If a gas is evolved it may indicate:— *Reactions with dilute $H_2SO_4$.*

| CARBONATES: | The gas is $CO_2$ | It is odorless and renders lime-water milky. |
| SULPHITES: | " " $SO_2$ | It smells of burnt sulphur and turns a solution of $BaCl_2$ and Br water turbid. |
| THIOSULPHATES: | " " $SO_2$ | As with sulphites, but sulphur is set free. |
| SULPHIDES: | " " $H_2S$ | It has a characteristic odor and blackens lead paper. |
| NITRITES: | " " $N_2O_3$ | Brown fumes. |
| HYPOCHLORITES AND CHLORITES: | " " $Cl_2$ | Yellow gas, characteristic odor. |
| SIMPLE CYANIDES: | " " $HCN$ | Colorless vapour of characteristic odor, precipitates solution of $AgNO_3$. |

SILICATES: No gas liberated, but in some cases the solution gelatinizes.

Then boil the mixture, if necessary, until odorless and, when cold, add twice its volume of concentrated sulphuric acid. Observe any reaction that occurs either at once or on heating *Reactions with concentrated $H_2SO_4$.*

to the boiling point. The following bodies exhibit characteristic phenomena.

Reactions with concentrated $H_2SO_4$.

OXALATES: . . . Give $CO_2$ and CO, turns lime-water milky.

CHLORIDES: . . . . " HCl, turns silver nitrate milky.

BROMIDES: . . . . . " HBr, and Br, gas is brownish, bleaches indigo and precipitates silver nitrate.

IODIDES: . . . . . . " iodine, violet vapours.

NITRATES: . . . . . " occasionally light brown vapours, strongly acid.

CHLORATES: . . . " $Cl_2O_4$, bright yellow, explosive gas.

ACETATES: . . . " odor of acetic acid.

COMPOUND CYANIDES: " CO, burns with pale blue flame.

SULPHOCYANATES: . " COS, peculiar odor. Burns with blue flame giving odor of $SO_2$.

FLUORIDES: . . . " HF, a colorless, suffocating gas which etches the tube.[1]

ORGANIC MATTER: . Substance turns black or brown.

SILICATES: . . . . · The substance gelatinizes (but not in all cases).

## EXAMINATION FOR THE ACIDS.

### GENERAL REMARKS.

**306.** It is impracticable to reduce the examination for the acids to so complete a system as that which is followed in detecting the bases, or to arrange any course of procedure, System. which would enable us test for all the acids consecutively in one portion of the solution. Instead of this, it is in general necessary to test different portions of the material for the various acids. Nevertheless, by following a systematic and

---

[1] The etching can often be seen only after the tube is washed and dried.

lies exhibit charac-

O, turns lime-water

ilver nitrate milky.

r, gas is brownish,
digo and precipitates
te.

vapours.

light brown vapours,
cid.

t yellow, explosive

ic acid.

with pale blue flame.

iar odor. Burns with
e giving odor of $SO_2$.

rless, suffocating gas
hes the tube.[1]

black or brown.

gelatinizes (but not in
.

ACIDS.

s.

e examination for the
which is followed in
course of procedure,
acids consecutively in
of this, it is in general
the material for the
ing a systematic and

be is washed and dried.

orderly mode of procedure, the results are both more certain
and more quickly reached.

Two different schemes are to be followed, according to
whether a precipitate forms in the solution, when it is care-
fully neutralized with ammonia, or not. If no precipitate is
produced upon neutralization, we are thereby assured of the
absence from the solution of any salt insoluble in neutral solu-
tions (v. Table III). If, on the other hand, a precipitate
forms when the solution is made neutral,[1] the simplest plan is
to first remove all those bases which could form precipitates
with any of the acids present. We accordingly proceed as
follows.

Add enough ammonia to a portion of the solution to render
it just neutral. If no precipitate forms, pass to §307.

If a precipitate is formed, add to the main part of the solu-
tion a considerable excess of sodium carbonate and boil in a
porcelain dish. The precipitate will contain all the bases of
the second, third, fourth and fifth groups, and possibly, phos-
phoric acid. Filter the solution and test the filtrate for the
acids according to the following sections, beginning at §307.

Removal
of bases of
higher
groups.

Wash the precipitate until the washings no longer exhibit
an alkaline reaction and examine it for phosphoric acid, as
follows. Transfer it while yet moist to a test-tube and shake
with ammonium sulphide. Allow it to stand for some time in
a warm place, filter, boil the filtrate, filter from separated sul-
phur and then add ammonia, ammonium chloride and magne-
sium chloride (v. §211). The appearance of a colorless
crystalline precipitate indicates phosphoric acid. The confir-
matory test with $AgNO_3$ should be applied.

In testing for the acids of Groups I, III and V, the treatment
with sodium carbonate, described above, is not necessary and
in the case of Group V it is better to omit it.

### GROUP I.

**307.** Acidify a part of the solution slightly (§192) with
hydrochloric acid and add a drop of barium chloride. If a

[1] The best means of ascertaining the point of neutralization is by the use of
lacmoid paper (§24).

Sulphuric acid; its detection and removal.

white, finely divided precipitate forms, *sulphuric acid* is present. Should a precipitate be produced by hydrochloric acid, the solution must be filtered before adding the barium chloride.

If sulphuric acid is found, add barium chloride gradually until it produces no further precipitate. Filter, and test the filtrate by the addition of one more drop of barium chloride, to make sure that all the sulphuric acid is removed. Examine the clear filtrate for the acids of the second group according to the following paragraph.

## GROUP II.

**308.** Neutralize carefully with ammonia the solution from which sulphuric acid has been removed (or a part of the original solution (§306) in case it contained no sulphates) and add barium chloride, if it has not already been added in the operations of the foregoing section.

*If no precipitate forms, all acids of the second group are absent.*[1] Pass to §312.

*If a precipitate appears, some acid of the second group is present.* If the precipitate is yellow, a chromate is probably present, if colorless, absent.

Acids of the first division.

The preliminary sulphuric acid test (§305) will have shown whether any acids of the first division of this group are present and, if so, which of them; except in complex mixtures, when all must be sought for.

If the substance evolved a gas, when treated with dilute or concentrated sulphuric acid, it must be examined for all acids of Division I, according to §§194 to 209, unless the preliminary examination gave unmistakable indications as to which are present and which absent.

Acids of the second division.

In either case, examine a portion of the original solution (or that treated with sodium carbonate, §306) as follows, for acids of Division II, bearing in mind that a chromate would have

---

[1]Carbonic acid may have been expelled and lost during the operation of separating the sulphuric acid. This is of no practical importance, since, if present, it would have been detected by the "Sulphuric Acid Test" during the preliminary examination.

, *sulphuric acid* is
ced by hydrochloric
adding the barium

chloride gradually
Filter, and test the
of barium choride, to
removed. Examine
d group according to

nonia the solution from
(or a part of the orig-
no sulphates) and add
en added in the opera-

*the second group are*

*of the second group is*
chromate is probably

(§305) will have shown
f this group are present
omplex mixtures, when

en treated with dilute or
examined for all acids
, unless the preliminary
ations as to which are

the original solution (or
o6) as follows, for acids
chromate would have

been indicated by the color of the precipitate, and the pre-
liminary examination would have revealed the presence of
silicates, unless present only in minute quantity.

**309.** If the preliminary examination (§305) showed the
presence of a silicate, the silicic acid must be removed by the
method given in §230. Since small amounts of $SiO_2$ may be
overlooked by the method of §305, it is desirable, in exact
analyses to carry out the process of §230 in *all* cases.   Silicates.

The solution filtered from the insoluble silica is to be used
for the following reactions.

**310.** Neutralize the solution, free from silicic acid, with   Phosphates.
ammonia,[1] add magnesium chloride and then an excess of
ammonia. Allow it to stand for several hours. A colorless,
crystalline precipitate indicates a phosphate or an arsenate
(§§212–216). To distinguish between them, filter, wash the
precipitate thoroughly and moisten it with silver nitrate solu-   Arsenates.
tion. If it turns *yellow* a *phosphate* is present, if *brick-red*, an
*arsenate.*

**311.** Test a portion of the original solution for *boric* acid
by §225 or §226.   Borates.

### GROUP III.

**312.** Acidify a portion of the original solution, or that
which was treated with sodium carbonate by §306, with dilute
nitric acid and add a drop of silver nitrate.

*If no precipitate forms, all acids of the third group are
absent.* Pass to §321.

If a precipitate is produced, test for the acids of Divisions
I, II, III and IV of this group, as follows.

#### DIVISION I.

**313.** Acidify a portion of the solution with hydrochloric
acid and add ferric sulphate (§235).

If the solution does not change color, *no acid of this division
is present.* Pass to §314.

---

[1] Ammonium chloride must be added if it is not already present; but if a
hydrochloric acid solution has been neutralized with ammonia, further addition
of an ammonium salt is usually superfluous.

If it becomes *red* a *sulphocyanate* is present; if *deep blue*, a
Compound *ferrocyanide.* If it turns reddish brown, add ferrous sulphate
cyanides. which will produce a *deep blue* in the presence of a *ferri-
cyanide.*

### Division II.

**314.** Mix a portion of the solution with a few drops of
dilute indigo solution, then add a considerable excess of dilute
sulphuric acid and boil (§246). If the indigo does not lose
its color, *acids of this division are absent.* Pass to §316.

If the indigo is bleached, proceed as follows.

Render a portion of the original solution slightly alkaline
Hypo- with sodium carbonate and add dilute indigo solution. If it
chlorites. is bleached, a *hypochlorite* is indicated. Confirm by one or
more of the tests given in §§247-249.

Regard must be had to the possible presence of a free
haloid (§§251–258).

**315.** Add a few drops of *dilute* sulphuric acid to a solu-
tion of ferrous sulphate, then add cautiously a portion of the
Nitrites. original solution, so as to form a separate layer. A brown
ring will be visible at the juncture of the two layers, if a
*nitrite* is present. (Compare §294).

Ferrocyanides and ferricyanides interfere with this reaction.

If the test of §314 gave a positive result (*i. e.* if indigo solu-
tion was bleached) and if the tests for hypochlorites and
Chlorites. nitrites gave negative results, a *chlorite* may be assumed to be
present. Confirm this conclusion by the reactions of §249.

### Division III.

**316.** If any acids of this division are present, the precipi-
tate produced by silver nitrate (§312) will be black or, in the
case of thiosulphates, will gradually become black on standing
Sulphides. or, more quickly, on boiling. The individual salts of the acids
of this division, if present, may be detected by the reactions
described in §§260 to 268, but a normal sulphide can not be
detected in the presence of a polysulphide.

When thiosulphates and sulphides are present together, the
Thiosul- latter must be removed before the former can be detected
phates. with certainty. To do this, add ammonia to a solution of zinc

sent; if *deep blue*, a
dd ferrous sulphate
resence of a *ferri-*

with a few drops of
rable excess of dilute
ndigo does not lose
Pass to §316.
lows.
tion slightly alkaline
ndigo solution. If it
Confirm by one or

e presence of a free

lphuric acid to a solu-
ously a portion of the
rate layer. A brown
f the two layers, if a

fere with this reaction.
ult (*i. e.* if indigo solu-
for hypochlorites and
may be assumed to be
e reactions of §249.

re present, the precipi-
will be black or, in the
ome black on standing
vidual salts of the acids
tected by the reactions
i sulphide can not be
ide.
e present together, the
rmer can be detected
nia to a solution of zinc

chloride until the precipitate formed at first is just redissolved.
Treat a portion of the original solution with an excess of the
reagent so prepared and then filter from the precipitated zinc
sulphide. The filtrate will be free from sulphides, but will
contain all the thiosulphuric acid originally present. The latter
can be detected by the reaction with hydrochloric acid (§266)
or, in the absence of other reducing agents, by that with
iodine (§268).

### DIVISION IV.

**317.** The detection of chlorides, bromides, iodides, and
cyanides, when present together in a solution, is a difficult  *Haloid salts.*
matter. When any one of these compounds is present it may
readily be detected by the tests given in §269 *et seq*.

In case it is desired to test for all of these compounds, in
solutions containing two or more of them, you may proceed as
follows:

Acidify a portion of the original solution with acetic acid and
heat to boiling. In the escaping vapours hold a drop of silver  *Cyanides.*
nitrate, suspended on a glass rod, or pass the evolved gas into
a silver solution. If a precipitate of silver cyanide is formed
in the silver nitrate solution, a *cyanide* is indicated. In this
case continue the boiling until the hydrocyanic acid, HCN, is
entirely expelled. Then add a small quantity of dilute sul-
phuric acid and an excess of ferric sulphate. If *iodine* is  *Iodides.*
present, it will be liberated and will make itself apparent by
the color of the evolved vapour and by its odor and, further,
by the starch paste reaction (§259).

In case iodine is found, boil the solution continuously until
it is entirely expelled.

The solution will now contain bromides and chlorides and
will be free from cyanides and iodides. If a precipitate is
formed during the boiling, filter. Divide the filtrate into two  *Bromides.*
portions: test one portion for bromides by §274; to the other
portion add silver nitrate. If a perfectly white precipitate
forms, which turns violet on exposure to the light a *chloride* is
present. If bromides are present this precipitate will be
yellowish. Usually, however, silver chloride can be detected

Chlorides. in the presence of a moderate amount of silver bromide by the action of light upon the former. In cases of uncertainty you may have to test a portion of the solution for chlorides according to §272. It is very difficult to detect a small quantity of a chloride in the presence of a large amount of bromides.

#### DETECTION OF CHLORIDES IN PRESENCE OF CYANIDES, FERROCYANIDES, SULPHOCYANATES AND FERRICYANIDES.

**318.** The presence of simple and compound cyanides prevents the recognition of chlorine by the silver nitrate test. A chloride may however be detected, in the presence of these cyanides, by boiling the precipitate produced by nitrate of silver for some time with concentrated nitric acid. Under this treatment all the cyanides will finally be decomposed and dissolved, silver chloride alone remaining undissolved.

#### DETECTION OF THE ACIDS OF DIVISION IV IN THE PRESENCE OF SULPHIDES.

Removal of sulphides. **319.** When a sulphide or a polysulphide is present in a solution containing a chloride, bromide or iodide, or all of these, it must be got rid of before the latter can be detected. For this purpose, add to the solution ferrous sulphate in slight excess, then ammonia in excess, boil for some time in an open dish and filter.

Detection of cyanides. The filtrate will be free from sulphides and can be directly tested for chlorides, bromides and iodides in the usual way. In employing this process, it is to be remembered that, if the original solution contained a simple cyanide, this will be converted into a ferrocyanide by the treatment described. It will be detected on acidifying the filtrate and adding a little ferric sulphate (§97) which will produce a precipitate of Prussian blue. This is the best way of detecting a cyanide in such mixtures.

#### GROUP IV.

**320.** If tartaric acid were present in the substance under examination, the preliminary test with concentrated sulphuric acid (§305) would have indicated organic matter by turning the substance black. In this case the special tests for tartrates (§§286–287) may be applied, otherwise they may safely be omitted.

lver bromide by the
of uncertainty you
ution for chlorides
detect a small quan-
amount of bromides.

NIDES, FERROCYANIDES,
ANIDES.

compound cyanides
he silver nitrate test.
the presence of these
duced by nitrate of
nitric acid. Under
be decomposed and
undissolved.

IN THE PRESENCE OF

phide is present in a
or iodide, or all of
atter can be detected.
rous sulphate in slight
some time in an open

s and can be directly
es in the usual wa.
membered that, if the
anide, this will be con-
ent described. It will
adding a little ferric
precipitate of Prussian
ng a cyanide in such

in the substance under
concentrated sulphuric
nic matter by turning
ecial tests for tartrates
they may safely be

## GROUP V.

**321.** Except in some complex mixtures, nitrates, chlo-rates and acetates are usually detected in the course of the preliminary examination. But since the detection of acetates (§305) depends upon the production of an odor, it may easily be understood that the presence of nitrites, nitrates, chlorates, hypochlorites, sulphides, sulphites, thiosulphates, chlorides, bromides, iodides, and other substances which evolve a pow-erful odor under the action of concentrated sulphuric acid, interfere more or less seriously with the acetic acid reaction.

The acids of the third group may be removed by treating the solution with silver sulphate in excess and filtering. From the filtrate the acids of the first and second groups may, similarly, be removed by treatment with barium hydrate and subsequent filtration. This filtrate will probably be very dilute. It must be boiled down to a small volume, and can then be tested for acetates (§290) which will be readily detected, unless nitrates or chlorates are also present. In the latter case, the formation of basic ferric acetate (§99), may be used to separate the acetic acid from the nitrates and chlorates. The basic acetate which will be precipitated on boiling the neutral solution with ferric chloride (containing no free acid) can be washed and used for the test of §290.

*Separation of acetates, chlorates, and nitrates from other salts.*

In case only one of the acids of this group is present, the reactions of §§290 to 300 will suffice for its easy detection or for confirmation if the preliminary examination gave an indi-cation.

## SYSTEMATIC COURSE OF ANALYSIS FOR THE DETECTION OF THE BASES.

### GENERAL REMARKS.

**322.** In the systematic course of analysis for the detec-tion of the bases, there are first separated, in groups (§25), from one another, by the aid of the general group-reagents. The individual bases of each group are then separated one from another by special methods, detailed in the following pages.

**323.** In order to make the general principles of the procedure clear, the following outline plan for the separation of the groups is presented.

*1.* Acidify the solution with hydrochloric acid and add hydrogen sulphide in excess.

> Groups V and VI are precipitated as sulphides.
> Filter and wash.   The filtrate contains Groups
> I, II, III and IV.   Pass to *2.*
>
>> Digest the precipitate with yellow ammonium
>> sulphide, filter and wash.   The filtrate contains
>> Group VI, the precipitate Group V.

*2.* Add ammonium chloride, then ammonia until alkaline, then ammonium sulphide.

> The precipitate contains Group III as hydrates
> and Group IV as sulphides.   The filtrate contains Groups I and II.   Pass to *3.*
>
>> Treat the precipitate with dilute hydrochloric
>> acid.   The residue contains **Ni, Co.**   Boil the
>> solution with excess of potassium hydrate.   The
>> precipitate contains **Fe, Mn, Cr.**   The filtrate
>> contains **Al, Zn.**

*3.* Add ammonium carbonate.

> The precipitate contains carbonates of Group II,
> EXCEPT MAGNESIUM.
>
>> The filtrate contains MAGNESIUM and Group I.
>> Add ammonium phosphate.   The precipitate
>> contains **Mg,** the filtrate, **Na** and **K.**

### SEPARATION OF GROUPS V AND VI FROM LOWER GROUPS.

**324.** Take a portion of the solution which has been reserved for the detection of the bases[1] and observe its odor

---

[1] Silicic or hydrofluoric acids, if originally present, must be removed before proceeding to the detection of the bases.   The methods of separation are given in §§228, 231.   (Cf. note to §330.)

rinciples of the pro-
or the separation of

c acid

as sulphides.
tains GROUPS

yellow ammonium
The filtrate contains
GROUP V.

mmonia

II as hydrates
e filtrate con-

h dilute hydrochloric
ns **Ni, Co**. Boil the
tassium hydrate. The
**In, Cr**. The filtrate

es of GROUP II,

NESIUM and GROUP I.
ate. The precipitate
**Na** and **K**.

VI FROM LOWER

tion which has been
and observe its odor

t, must be removed before
hods of separation are given

---

and reaction with litmus or, better, with lacmoid paper. If it
is very strongly acid, dilute it freely with water.[1] If neutral, Precipita-
acidify slightly with hydrochloric acid. Then, no matter tion of the
whether a precipitate forms or not, pass hydrogen sulphide heavy
through the solution until it smells strongly of the gas after metals.
shaking. If no colored precipitate appears, metals of the
higher groups are absent. Pass to §330.

If a precipitate forms, other than a finely divided, white one
of sulphur, it will contain the metals of the fifth and sixth
groups. Warm the solution nearly to boiling, filter and wash
as rapidly as possible with water containing a little hydrogen
sulphide. The filtrate ($A$) will contain any bases of the first,
second, third and fourth groups which may be present. Set
it aside for examination according to §330. The treatment of
the precipitate is given in the next paragraph.

#### SEPARATION OF THE FIFTH FROM THE SIXTH GROUP.

**325.** Punch a hole in the filter paper containing the pre- Treatment
cipitated sulphides and rinse the latter into a test-tube. Add of the pre-
to it a moderate quantity of yellow ammonium sulphide, shake with
thoroughly, warm gently without boiling and allow the whole ($NH_4$)$_2$S.
to digest for at least ten minutes. Filter and wash the precip-
itate with a warm, dilute solution of ammonium sulphide.
From time to time acidify successive portions of the filtrate
with hydrochloric acid and, when this produces a pure white
turbidity, begin to wash the precipitate with cold water, con-
tinuing the washing until the precipitate no longer smells of
ammonium sulphide.

The filtrate ($Aa$) contains the sulphides of arsenic, antimony,
tin, (gold and platinum); while the precipitate ($Bb$) consists of
sulphides of metals of the fifth group. (Pass to §327).

#### EXAMINATION OF THE AMMONIUM SULPHIDE SOLUTION (GROUP VI).

**326.** Add hydrochloric acid to filtrate $Aa$ (*v.* previous
paragraph) until it is distinctly, but not strongly acid. The

---

[1] If a precipitate forms at this point, it probably consists of a basic salt of
bismuth or antimony. In this case, filter, wash the precipitate and test it for
those bases (§§154, 179).

precipitate which forms will consist of sulphides of Group VI,
mixed with free sulphur. Boil, filter and wash slightly.
Transfer the precipitate to a porcelain dish, add an excess of
concentrated nitric acid and boil until half the acid is boiled
away. Dilute with water and boil again for one minute.
Globules of yellow sulphur may remain undissolved and, if so,

Tin and they should be removed.[1] If a white precipitate forms, it may
antimony. consist of metastannic acid or metantimonic acid[2] (§§162, 165,
179). It can be examined by the blow-pipe (§384).

Arsenic.     The solution may contain arsenic in the form of arsenic
acid, $H_3AsO_4$, and a little antimony as antimonic acid. Test
it according to §170 or §215 for arsenic.

Test a portion of the insoluble residue for tin by fusion on
charcoal under the reducing flame with sodium carbonate and
potassium cyanide mixture (§165). Digest another portion
with a small quantity of concentrated hydrochloric acid in a
porcelain dish. Dilute the solution with three times its bulk
of water and then, no matter whether the residue completely

Antimony. dissolves or not, introduce a fragment of pure zinc and a piece
of platinum foil *in contact* with one another. If antimony is
present, a black stain will appear on the platinum (§179).
Pour off the solution, filtering if necessary, and mix it with a
solution of mercuric chloride. If the latter is reduced, giving

Tin.      a white or gray precipitate of mercurous chloride or metallic
mercury (§125), tin is present.

If it is desired to test for gold and platinum, mix a portion
of the precipitated sulphides (*Bb*, §325) with sodium carbon-
ate and nitrate, and fuse in a porcelain crucible. The noble

Gold and  metals will alone be reduced. Boil the mixture with water,
platinum.  filter and wash. Boil the residue with concentrated hydro-
chloric acid. The portion still undissolved is gold or platinum.
If the former, it can be fused to a globule in the oxidizing

---

[1] If there should be any difficulty in deciding from its appearance whether the
undissolved residue consists *entirely* of sulphur, heat it on platinum foil. If
it first fuses and then burns away, it is nothing more than sulphur.

[2] If much metantimonic acid is present, it may carry down with it a part or
even the whole of the arsenic acid.

hides of Group VI,
and wash slightly.
sh, add an excess of
lf the acid is boiled
ain for one minute.
ndissolved and, if so,
cipitate forms, it may
ic acid³ (§§162, 165,
ipe (§384).

the form of arsenic
ntimonic acid. Test

e for tin by fusion on
sodium carbonate and
igest another portion
ydrochloric acid in a
three times its bulk
he residue completely
f pure zinc and a piece
other. If antimony is
the pla inum (§179).
ary, and mix it with a
tter is reduced, giving
us chloride or metallic

platinum, mix a portion
) with sodium carbon-
crucible. The noble
e mixture with water,
h concentrated hydro-
ved is gold or platinum.
lobule in the oxidizing

om its appearance whether the
heat it on platinum foil. If
ore than sulphur.

y carry down with it a part or

flame on charcoal. Dissolve the metal in *aqua regia* and, after
evaporating most of the acid, test the solution for gold (§197)
and for platinum (§183).

EXAMINATION OF THE PRECIPITATED SULPHIDES OF METALS OF GROUP V.

**327.** Transfer the precipitate (*Bb*, §325) containing $Ag_2S$,
$PbS$, $CuS$, $Bi_2S_3$, $HgS$, $CdS$, to a casserole, pour nitric acid
over it and boil for some time. The undissolved residue, if
any, consists merely of sulphur, if it is yellow, but, if dark
colored, it may contain mercury. In the latter case wash it, Mercury.
dissolve by boiling with a little bromine and water and test
for mercury according to §125.

**328.** The solution in nitric acid is to be cautiously evapo-
rated nearly to dryness, then freely diluted with water and
boiled. The appearance of a white precipitate indicates bis- Bismuth.
muth. Apply confirmatory test (§§152–154). Filter. Add
hydrochloric acid to the filtrate. Any silver present will be
precipitated as a silver chloride. A portion of the lead may
also be thrown down as lead chloride. Filter, wash the pre-
cipitate with boiling water, and test it for silver according to Silver.
§§116 and 118.

**329.** To the filtrate add a few drops of dilute sulphuric
acid. If a white precipitate forms, it consists of lead sulphate.
To remove the lead, add a considerable excess of dilute sul- Lead.
phuric acid. Filter, wash, and apply confirmatory tests to the
precipitate. (Compare §§131 and 135).

The filtrate from the lead sulphate, or the solution in which
sulphuric acid produced no precipitate, will contain copper
and cadmium, if these were present. Test one portion for
copper by the addition of potassium ferrocyanide, (§140). Copper.
If it is desired to test also for cadmium, proceed with a second
portion as follows. Add potassium sulphocyanate and sodium
sulphite (or sodium thiosulphate). Warm the solution, but
not to boiling, for five minutes. This will precipitate all the
copper as cuprous sulphocyanate, $Cu_2(SCN)_2$, leaving the
cadmium in solution. Filter and treat the filtrate with $H_2S$.
A yellow precipitate indicates cadmium (§156).

Cadmium may also be detected in the filtrate from the lead sulphate precipitate by treating it with hydrogen sulphide, then boiling and filtering. The cadmium sulphide will dis-
Cadmium. solve in the dilute sulphuric acid. Filter the solution from the insoluble CuS, nearly neutralize with ammonia and precipitate the cadmium with hydrogen sulphide.

### GROUPS I, II, III AND IV.

**330.** The filtrate, ($A$) from the hydrogen sulphide precipitate, or that in which hydrogen sulphide produced no precipitate (§324), is to be differently treated according to whether phosphoric, oxalic or boric acids are present or absent.

It should therefore next be tested for these acids, (§§203,
Removal 204, 211, 212, 224 to 226). If oxalic acid alone is found, add
of oxalates. to the solution a moderate quantity of concentrated sulphuric acid and evaporate until white fumes of sulphuric acid begin to appear. This treatment destroys the oxalic acid.

Then add water[1] and proceed with the solution according to the following section. If either phosphoric or boric (or silicic) acids are present; follow §338, *et seq*., otherwise §331.

### SEPARATION OF GROUPS III AND IV FROM GROUPS I AND II, WHEN PHOSPHORIC, OXALIC AND BORIC ACIDS ARE ABSENT.

Precipi- **331.** Add ammonia gradually until the solution is neutral,
tation by then add ammonium sulphide in slight excess. Warm gently,
ammonium filter and wash. If the filtrate has a tendency to run through
sulphide.

---

[1] If complete solution does not take place, the precipitate consists of barium sulphate, calcium sulphate, or strontium sulphate, or a mixture of these. After filtration and washing, this precipitate is to be examined for Ba, Sr, and Ca, (*vide* §§344, 353). Enough calcium sulphate will remain in solution to be detected in the regular course of analysis. If the precipitate gives dubious results for both strontium and barium by the flame test, boil it with sodium carbonate solution, filter and wash. Treat the precipitate, which now, probably, consists of barium sulphate and strontium carbonate, with dilute hydrochloric acid and filter the solution from the undissolved portion. If both barium and strontium are present, the solution will exhibit the flame reaction of the latter, whereas the precipitate will give the green flame of barium.

filtrate from the lead
hydrogen sulphide,
m sulphide will dis-
the solution from the
monia and precipitate

IV.

drogen sulphide pre-
ulphide produced no
treated according to
acids are present or

r these acids, (§§203,
cid alone is found, add
concentrated sulphuric
f sulphuric acid begin
e oxalic acid.
the solution according
osphoric or boric (or
*et seq.*, otherwise §331.

IV FROM GROUPS
, OXALIC AND
BSENT.

d the solution is neutral.
excess. Warm gently,
endency to run through

precipitate consists of barium
, or a mixture of these. After
examined for Ba, Sr, and Ca,
ll remain in solution to be
the precipitate gives dubious
me test, boil it with sodium
cipitate, which now, probably,
ate, with dilute hydrochloric
ortion. If both barium and
e flame reaction of the latter,
of barium.

---

brown,[1] the addition of ammonium chloride to the water used
for washing is advisable. The filtrate ($C$) contains bases of
Groups I and II. Pass to §342.

**332.** The precipitate ($D$) may contain aluminium hy- <span style="float:right">Indications<br>from color<br>of the pre-<br>cipitate.</span>
drate, chromium hydrate, manganese sulphide, ferrous sulphide,
zinc sulphide, nickel sulphide, cobalt sulphide. The color of
this precipitate should be carefully observed.

If it is white, pale green or flesh-colored, nickel, cobalt
and iron must be absent. In this case omit the tests for these
bases and pass directly to §335. Should the precipitate be
darker in color, all the metals of Groups III and IV may be
present.

SEPARATION OF NICKEL AND COBALT FROM THE OTHER METALS
OF THIS GROUP.

**333.** Rinse the precipitate $D$ (previous section) into a
small flask, add dilute hydrochloric acid, shake thoroughly,
and allow to stand in the cold for at least ten minutes.

If the precipitate dissolves entirely, with the exception of
flakes of sulphur, nickel and cobalt are absent. (Pass to
§335).

If there is an undissolved black residue, filter and wash.

The filtrate ($E$) is to be examined according to §335.

Test the precipitate in the borax bead in the oxidizing flame <span style="float:right">Nickel and<br>cobalt in<br>the borax<br>bead.</span>
for nickel and cobalt (§§ 9, 78, 84).

Should the precipitate be too small in quantity to remove
from the filter paper, tear off the apex of the filter with the
precipitate, wrap it, while still moist, around the borax bead
and expose to the oxidizing flame.

The filter paper will rapidly burn away and the precipitate
will dissolve in the borax.

If the bead is blue in the oxidizing and in the reducing
flame, cobalt is present (§78), but if brown in the oxidizing
flame and colorless to gray in the reducing flame, nickel
(§84).

If on the contrary the bead is clear blue in the reducing

---

[1]This is only likely to occur when nickel is present.
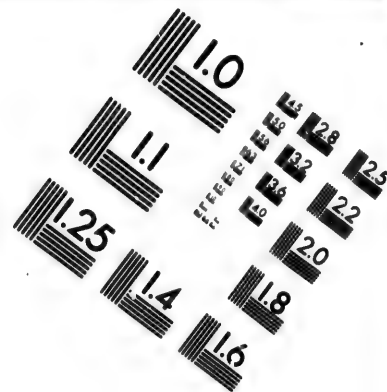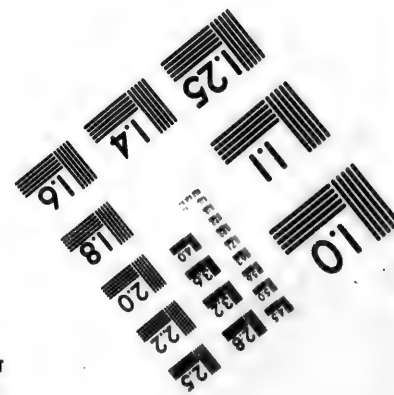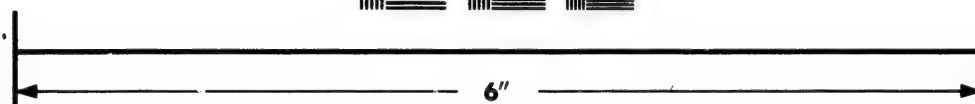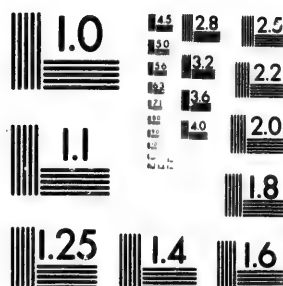
# IMAGE EVALUATION
# TEST TARGET (MT-3)

6"

Photographic
Sciences
Corporation

23 WEST MAIN STREET
WEBSTER, N.Y. 14580
(716) 872-4503

# CIHM/ICMH
## Microfiche
## Series.

# CIHM/ICMH
## Collection de
## microfiches.

© 1981

flame but dirty blue in the oxidizing flame, both cobalt and nickel may be suspected.

**334.** Often when both nickel and cobalt are present, they can not be distinguished from one another by their behaviour in the borax bead. In such cases they may be separated by the following process.

Precipitation of cobalt with $KNO_2$.
Dissolve the precipitate ($D$, §332) in a small quantity of hot, concentrated hydrochloric acid. Add potassium acetate and potassium nitrite, $KNO_2$, in excess, and allow to stand in a warm place for some time. Cobalt appears as a yellow precipitate of potassium cobaltic nitrite, $K_3Co(NO_2)_6$, (§80). Filter, evaporate the filtrate to dryness and test the residue by the borax bead, in the oxidizing flame, for nickel (§84).

**335.** The filtrate ($E$, §333) from the sulphides of nickel and cobalt is to be boiled to expel $H_2S$. Add bromine-water

Hydrates of Fe, Mn and Cr.
in slight excess and then sodium hydrate in considerable excess. Boil in a porcelain dish for one minute. The precipitate ($F$), if any, contains the iron, manganese and chromium.[1] Dilute, and filter. The filtrate ($G$) contains zinc and aluminium.

**336.** Examine the precipitate ($F$) for iron, manganese and chromium (*and also for zinc, if chromium is found*) as follows:

Iron.
Dissolve a small portion in dilute hydrochloric acid and test it with KSCN or $K_4Fe(CN)_6$ for iron (§§97, 98).

Manganese.
Test another portion for manganese in the borax bead or sodium carbonate bead (§§106, 107).

Chromium.
Mix the greater portion of the precipitate with sodium carbonate and sodium nitrate (see §71, $a$). Fuse on platinum foil for one minute. Dissolve the melt in water and, if the solution is green, boil it with a few drops of alcohol and filter. If the filtrate is yellow, chromium is present. Acidify the filtrate with acetic acid. *If yellow*, divide it into two parts. To one part add lead acetate, as confirmatory test for chromium (§71, $a$). To the other part add potassium ferrocyanide. A white precipitate indicates zinc (§112).

---

[1] If much chromium is present, this precipitate may also contain a part or the whole of the zinc.

me, both cobalt and

cobalt are present,
e another by their
cases they may be

a small quantity of
d potassium acetate
, and allow to stand
appears as a yellow
$K_6Co(NO_2)_6$, (§80).
d test the residue by
r nickel (§84).
e sulphides of nickel
Add bromine-water
n considerable excess.
The precipitate (*F*),
chromium.[1] Dilute,
c and aluminium.

for iron, manganese
*hromium is found*) as

ochloric acid and test
§§97, 98).
in the borax bead or

tate with sodium car-
Fuse on platinum
in water and, if the
s of alcohol and filter.
present. Acidify the
ide it into two parts.
matory test for chro-
d potassium ferrocy-
c (§112).

may also contain a part or

**337.** Examine filtrate *G* (§335) for aluminium and zinc as follows. Acidify slightly with hydrochloric acid; add ammonia in considerable excess (§64). Let it stand for ten **Aluminium.** minutes. The formation of a white precipitate (*H*) indicates aluminium. Filter and wash. Test the filtrate for zinc with **Zinc.** ammonium sulphide (§111). A white precipitate indicates zinc.[1]

Transfer a part, or the whole, of the precipitate (*H*) to a charcoal stick; ignite in the oxidizing flame and test with cobalt nitrate for aluminium[2] (§64).

#### EXAMINATION OF GROUPS III AND IV, IN PRESENCE OF PHOSPHATES, BORATES OR SILICATES.

**338.** When, of these acids, silicic acid alone is present, it may be removed by the processes described in §§228 or 231, **SiO₂ must** and the residual solution then analyzed in the usual way.[3] **be removed.**

**339.** Phosphoric or boric acids having been found, proceed as follows with the solution (*A*, §324).

Boil to expel hydrogen sulphide, add bromine-water in slight **Removal** excess, and boil to expel the excess. Test a small sample of **of phos-** the solution for iron (§97). Add ferric chloride and then **phates and** ammonia in excess. The precipitate should be *brown*. If it **borates.** is *white*, this shows that not enough ferric chloride has been added to combine with all the phosphoric acid. Add an additional amount of ferric chloride in this case, then acidify cautiously with acetic acid. Boil for three minutes, filter and wash. The precipitate (*I*) contains the phosphoric acid (or boric acid) in combination with iron, and all the rest of the **Basic** iron, the chromium and the aluminium as basic acetates. Pass **acetate** to §§340, 341. **method.**

---

[1] Confirmatory test, §109.

[2] This confirmatory test for aluminium should never be omitted.

[3] If the solution contains fluorides, it may be treated as described in the following section. The process there described removes the hydrofluoric acid in the form of basic ferric fluoride. Or, the solution may be evaporated to dryness and then heated to a high temperature with an excess of concentrated sulphuric acid until the HF is all expelled. Since solutions containing fluorides can not be analyzed in glass vessels, it is seldom necessary in qualitative analyses for practice to remove this acid.

**340.** The filtrate ( $\mathcal{J}$ ) contains the remaining bases of Groups IV and those of II and i. Proceed with the examination of this filtrate ( $\mathcal{J}$ ) in the usual way, beginning at §331, but omitting all that relates to the tests for iron.

Detection of Al and Cr.
**341.** Transfer the precipitate ( $I$ , §339) to a porcelain dish, add sodium hydrate, boil and filter. Test the filtrate for aluminium by §337 and the precipitate for chromium *by fusion with sodium carbonate and nitrate, etc.* (§71, *a*).

SEPARATION OF THE SECOND GROUP FROM THE FIRST.

Precipitation by $(NH_4)_2CO_3$.
**342.** Boil the solution (filtrate *C*, §331) from which bases of the higher groups have been removed, until it no longer smells of ammonium sulphide; add ammonium chloride and then ammonium carbonate in slight excess. Warm gently, but not to boiling. If a precipitate ( $K$ ) forms, it m' *j* contain the carbonates of calcium, barium and strontium. (Pass to §344 or 345). Filter and wash.

Magnesium.
**343.** The filtrate ( $L$ ) contains magnesium, sodium and potassium, if these are present. Divide it into two parts. Test one part with sodium phosphate and ammonia according to §61, for magnesium. Only when a *crystalline* precipitate forms at this point, can you safely conclude that magnesium is present.

Test the other portion of filtrate ( $L$ ) for sodium and potassium (§346).

THE SEPARATION AND DETECTION OF BARIUM, STRONTIUM AND CALCIUM.

**344.** Dissolve the precipitate ( $K$ ) in the least possible quantity of dilute, hot hydrochloric acid. Dip a clean platinum wire in the solution obtained and hold it in the Bunsen flame. An orange color indicates calcium (§43); scarlet, strontium (§47); or green, barium (§51).

Precipitation by $CaSO_4$.
Divide this solution ( $M$ ) into two parts. To one part add a solution of calcium sulphate. If a precipitate forms at once, *barium* is present. If it forms only after standing for some time, *strontium* is indicated. In either case filter, wash and apply confirmatory flame test to the precipitate. Should no

remaining bases of
ed with the examina-
y, beginning at §3;1,
r iron.

§339) to a porcelain
Test the filtrate for
r chromium *by fusion*
§71, *a*).

P FROM THE FIRST.

, §331) from which
removed, until it no
d ammonium chloride
xcess.  Warm gently,
forms, it m' *j* contain
strontium.  (Pass to

agnesium, sodium and
ide it into two parts.
nd ammonia according
*crystalline* precipitate
lude that magnesium is

for sodium and potas-

IUM, STRONTIUM AND

) in the least possible
Dip a clean platinum
it in the Bunsen flame.
43) ; scarlet, strontium

rts.  To one part add
ecipitate forms at once,
ter standing for some
r case filter, wash and
recipitate.  Should no

---

precipitate form, barium and strontium are both absent.  In this case, test the second portion of solution *M* for calcium, as given below.

If the examination above has shown the presence of barium or strontium, add dilute sulphuric acid to the second portion of the solution ( *M* ) until no further precipitate ( *Mm* ) forms.  Filter and wash.  Neutralize the filtrate with ammonia, then add ammonium oxalate.  The formation of a precipitate indicates calcium, (§46).  Apply confirmatory flame test.  **Calcium.**

The precipitate *Mm*, which may consist of a mixture of the sulphates of barium and strontium or of either of these salts alone, should be examined for both metals by the method described in the last part of §353.  It is necessary to do this, even when the flame test seems to show that only one of the metals is present, for the reason that either of the two bases if present in large excess may obscure the flame reaction of the other.  **Barium.**  **Strontium.**

SECOND METHOD FOR THE SEPARATION AND DETECTION OF CALCIUM, STRONTIUM AND BARIUM.

**345.**  The method just described does not always give, in inexperienced hands, satisfactory results, when strontium and barium are both present.  The following process may be used instead.

Neutralize the hydrochloric acid solution of the carbonates ( *M*, §344) with ammonia, acidify *slightly* with acetic acid and add potassium pyrochromate in excess.  The appearance of a pale yellow precipitate ( *N* )[1] indicates *barium*.  Filter and test the filtrate ( *O* ) with a drop of dilute sulphuric acid for strontium (§48).  If a white precipitate forms, it consists of strontium sulphate.  In this case, add sulphuric acid drop by drop until no further precipitate forms, filter, neutralize the filtrate with ammonia and add ammonium oxalate.  The appearance of a white precipitate, of calcium oxalate, indicates calcium (§46).  Apply confirmatory test.  **Removal of barium as $BaCrO_4$**

---

[1] The precipitate N, consisting of barium chromate, may be moistened with HCl and tested on a platinum wire in the flame (§51).

### DETECTION OF THE BASES OF GROUP I.

Sodium and potassium.

**346.** The solution ($L$, §343) may be directly tested for sodium and potassium by the flame test or by either of the reactions given in §§30, 33, 34 and 35.

**347.** Ammonium salts must be tested for in a portion of the original solution. To this end, add potassium hydrate or sodium hydrate in excess and warm the solution. If the escaping vapours smell of ammonia and exhibit an alkaline reaction, an ammonium compound is present (§38).

Ammonium.

## EXAMINATION OF INSOLUBLE SUBSTANCES.

Solution of non-metallic solids.

**348.** If the substance under examination is a solid, it must be brought into solution for analysis. It should be dissolved in water if possible. If insoluble in water and non-metallic,[1] treat it with dilute hydrochloric acid. If insoluble even on warming, heat it with dilute nitric acid. If insoluble in this menstruum also, try *aqua regia*.[2] If it dissolves, dilute the solution with water and boil to expel chlorine. If the substance is dissolved by either of these modes of treatment the solution may be analyzed by the methods already given.

**349.** If the substance is insoluble in hydrochloric acid, nitric acid or *aqua regia*, it is probably one of the bodies enumerated in the following list:

| | |
|---|---|
| Sulphur. | Silver Chloride. |
| Carbon. | Silver Bromide. |
| Barium Sulphate. | Silver Iodide. |
| Strontium Sulphate. | Stannic Oxide. |
| Lead Sulphate. | Silica. |
| Aluminium Oxide. | Many Silicates. |
| Chromium Oxide. | Compound Cyanides. |

Some clue as to the nature of the substance will have been obtained in the preliminary examination, and the methods given below will be found useful for its complete identification.

---

[1] If it is metallic, follow §§382, 383, or Table I, p. 104.

[2] Four parts strong hydrochloric, one part strong nitric acids.

ROUP I.

e directly tested for
or by either of the

d for in a portion of
otassium hydrate or
he solution.  If the
d exhibit an alkaline
sent (§38).

SUBSTANCES.

ation is a solid, it must
It should be dissolved
ter and non-metallic,[1]
If insoluble even on
If insoluble in this
it dissolves, dilute the
chlorine.  If the sub-
hodes of treatment the
ds already given.
e in hydrochloric acid,
bly one of the bodies

hloride.
romide.
odide.
Oxide.

ilicates.
nd Cyanides.
bstance will have been
ion, and the methods
complete identification.

. 104.
g nitric acids.

**350.** SULPHUR.  Crystalline sulphur, although soluble on continued boiling with nitric acid, forming sulphuric acid, may be met with here.  If heated on platinum foil, it burns with a characteristic blue flame, without leaving any residue.  If boiled with sodium hydrate and a silver coin, the latter will be blackened.

**351.** CARBON.  Carbon in some of its forms, as gas-retort carbon or as graphite, is almost insoluble in boiling nitric acid.  Its combustibility by prolonged heating in the oxidizing flame and its physical properties serve for its identification.
*Combustibility of carbon.*

In case much carbon is intimately mixed with relatively small quantities of other substances, as in the carbon sticks employed in the production of the electric arc light, the carbon hinders the solubility in acids of other constituents.  The latter must, accordingly, be detected in the ash, after burning away the carbon.  To this end, pulverize the material finely, spread it in a thin layer over a sheet of platinum and heat the latter to incandescence with the Bunsen flame.  The carbon will slowly be consumed.  The ash is to be analyzed as directed for silicates, §357.
*Analysis of ash.*

**352.** BARIUM SULPHATE.  Barium sulphate gives a green flame coloration, and the sulphur reaction when fused on charcoal with sodium carbonate (§193).

In mixtures of lead sulphate with barium sulphate the former may be separated by taking advantage of its solubility in a solution of ammonium acetate in strong ammonia.  The barium sulphate will remain undissolved and may then be readily recognized by the flame reaction, etc., which would have been difficult before the removal of the lead sulphate.
*Separation of PbSO₄ from BaSO₄*

**353.** STRONTIUM SULPHATE gives the strontium flame, and the sulphur reaction.  If fused with sodium carbonate on platinum foil, it is decomposed as follows:

$$SrSO_4 + Na_2CO_3 = SrCO_3 + Na_2SO_4$$
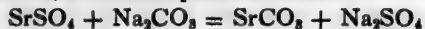
Boil the melt with water, filter; test the filtrate for sulphuric acid (§307).  Dissolve the precipitate in dilute nitric acid and test for strontium (§§47, 48).

Mixtures of BaSO₄ and SrSO₄.

If the substance consists of a mixture of strontium sulphate with barium sulphate, both bases may be detected by the following procedure.

Boil the mixture with an excess of a dilute solution of sodium carbonate. This converts most of the strontium sulphate into strontium carbonate, but has little effect upon the barium sulphate. Filter the solution and wash the precipitate until no longer alkaline. Treat the precipitate with warm, hydrochloric acid, filter, and wash. The solution will contain the strontium and is to be tested for it by the flame reaction, while the barium may be detected in the same way in the undissolved portion of the precipitate.

**354.** LEAD SULPHATE turns black on treatment with ammonium sulphide. It affords globules of lead when fused on charcoal. It may be brought into solution in the same way as strontium sulphate, §353. (Compare §352).

**355.** SILVER CHLORIDE, BROMIDE AND IODIDE may be recognized by their properties as given in §§116, 117, 118.

Reduction of Insoluble silver salts.

If it is suspected that the insoluble substance may contain two of these silver salts, or all three, mix it with its own weight of dry sodium carbonate and fuse in a porcelain crucible. Extract the residue with water and examine the solution for iodides, bromides and chlorides (§317).

Another method of separating the haloids from their insoluble compounds with silver, is to digest the substance, which perhaps contains AgCl, AgBr and AgI, with fresh ammonium sulphide for an hour or two. Finally, boil and filter. The precipitate contains the silver as sulphide, while the haloids are present in the form of ammonium salts in the filtrate, where they may easily be detected (*l. c.*).

**356.** STANNIC OXIDE, OR METASTANNIC ACID, (*v.* §§162 to 165). It may be brought into solution as potassium stannate, $K_2SnO_3$, by fusion with potassium carbonate and treatment with water.

If metastannic acid is mixed with the insoluble compounds mentioned above (§§351 to 355), it may be isolated by taking advantage of its solubility in *yellow* ammonium sulphide.

strontium sulphate
oe detected by the

a dilute solution of
f the strontium sul-
ittle effect upon the
wash the precipitate
ecipitate with warm,
solution will contain
y the flame reaction,
the same way in the

on treatment with
s of lead when fused
lution in the same way
§352).

AND IODIDE may be
in §§116, 117, 118.
ubstance may contain
, mix it with its own
se in a porcelain cruci-
d examine the solution
7).

loids from their insolu-
t the substance, which
, with fresh ammonium
, boil and filter. The
le, while the haloids are
s in the filtrate, where

ANNIC ACID, (v. §§162
ion as potassium stan-
n carbonate and treat-

he insoluble compounds
y be isolated by taking
ammonium sulphide.

Digest it over night with a considerable excess of the reagent
named, then filter and wash. Sometimes several repetitions
of the digestion will be requisite to entire'y remove the tin.
The filtrate will contain the tin as ammonium sulphostannate,
and acidification with hydrochloric acid will precipitate it as
stannic sulphide (§§160, 165).

357. SILICA. (See §§228, 230 and 231). Silicates may
be recognized by fusion with the microcosmic salt bead, §232. Analysis
Silica and many of its compounds, when finely pulverized and of silicates.
heated before the blowpipe, after moistening with cobalt nitrate
solution, become *pale blue*. (Cf. §64).

In order to prepare a silicate for analysis, it should be finely
pulverized and mixed with five times its weight of dry sodium
carbonate and about one-tenth its weight of sodium nitrate,
and the mixture fused thoroughly on platinum foil or in a
platinum crucible. Boil the fused mass with water until it is
softened. Acidify strongly with hydrochloric acid, evaporate
the solution to dryness and treat as directed in §228, to sepa-
rate the silicic acid. The filtered solution may then be
analyzed according to the general methods, bearing in mind
that it cannot be used for the detection of sodium and potas-
sium.

The latter may sometimes be detected by moistening the
finely powdered silicate with sulphuric acid and introducing
the mixture on the platinum wire into the flame, when the
characteristic yellow of sodium or violet of potassium may be
observed.

Another method of preparing silicates for analysis, and a
better one than the first described, in so far as it permits the Detection
detection of sodium and potassium with certainty, is dependent of alkalies
upon the expulsion of the silica in the form of silicon fluoride, in silicates.
$SiF_4$ (§231). Pulverize the silicate (about $\frac{1}{4}$ gram) finely
and digest with hydrofluoric acid in a platinum dish until com-
pletely decomposed. Then add about 1 c.c. of concentrated
sulphuric acid and heat until the water, hydrofluoric acid and
silicon fluoride are expelled. This point will be indicated by
the evolution of dense, white, suffocating vapour of sulphuric
acid. When cold, dilute with water. A white precipitate

may consist of barium sulphate (§352), strontium sulphate (§353), calcium sulphate (§44), lead sulphate (§§354, 131), or metastannic acid (§§162, 356). If a precipitate forms, filter and wash *thoroughly*. The filtrate may be analyzed in the regular way, omitting, of course, the tests for sulphuric acid, barium, strontium and lead.

**358.** COMPOUND CYANIDES. If an insoluble, compound cyanide be boiled for some time with concentrated sulphuric acid, the nitrogen of the cyanide will be converted into ammonium sulphate and in the solution the amnonia may be detected by §38 or §40, and the bases by the usual methods.[1]

*Conversion of cyanides into NH₃.*

**359.** ALUMINIUM OXIDE AND CHROMIUM OXIDE, after prolonged ignition, or when occurring as minerals, are often totally insoluble in the ordinary acids. They may be rendered soluble, after finely pulverizing, by prolonged fusion at a dull red heat with acid potassium sulphate, or by fusion with the oxidizing flux mentioned in §71, p. 21. The latter treatment will convert the alumina into sodium aluminate and the chromium oxide into sodium chromate. The alumina can be precipitated from the solution *after* filtration by §66, and its presence confirmed by §64. The filtrate from the aluminium hydrate can be used for the detection of the chromic acid.

### REMOVAL OF ORGANIC MATTER.

**360.** A substance containing organic matter is usually blackened by the application of heat; moisture and empyreumatic vapours being frequently evolved at the same time. When organic matter is found, it must be removed before proceeding to the analysis, because such matter interferes with many of the reactions of bases and acids. In case the bases and acids to be tested for are those which will stand a red heat without volatilization or decomposition, the best way to remove organic matter is to burn it off by ignition of the substance on platinum foil or in a crucible. Otherwise the

*Combustion.*

---

[1] This mode of examination does not show *what* compound cyanides are present, that being a difficult problem, the full discussion of which would exceed the limits of this work.

strontium sulphate
ate (§§354, 131), or
cipitate forms, filter
be analyzed in the
s for sulphuric acid,

insoluble, compound
ncentrated sulphuric
converted into ammo-
onia may be detect-
sual methods.[1]

ROMIUM OXIDE, after
as minerals, are often
They may be rendered
nged fusion at a dull
or by fusion with the
The latter treatment
minate and the chro-
The alumina can be
tration by §66, and its
te from the aluminium
the chromic acid.

MATTER.

nic matter is usually
moisture and empyreu-
ed at the same time.
st be removed before
matter interferes with
ls. In case the bases
which will stand a red
ition, the best way to
off by ignition of the
cible. Otherwise the

_hat_ compound cyanides are
discussion of which would

organic substances may be oxidized and destroyed by the fol-
lowing method, which is well suited for the detection of
arsenic, lead, mercury and other inorganic poisons in articles
of food, parts of the human body, etc.

Mix the material with an equal volume of concentrated
nitric acid, warm gently and throw into the mixture, while
warm, a little powdered potassium chlorate. Continue the **Oxidation of organic matter.**
heating for some time, adding occasionally potassium chlorate
in small quantities. Evaporate most of the nitric acid, dilute
with water and analyze the solution in the usual way. It
must be remembered that this treatment converts all sulphur
compounds present into sulphuric acid and, in general, most of
the elements into their highest state of oxidation. Iodine and
bromine are expelled, in part at least, with the escaping
vapours. These elements and chlorine may be detected by
heating the original substance with concentrated sulphuric
acid and passing the escaping vapour into water, in which
the hydrochloric, hydrobromic or hydriodic acid will dissolve
and in which they may be detected by the usual methods; the
sulphurous acid, evolved by the action of the sulphuric acid
on organic substances, sufficing to reduce any iodine which
might be liberated, back again to the form o hydriodic acid.

Any treatment which would destroy organic matters would **Detection of "prussic acid."**
also decompose hydrocyanic acid (or its salts), if present. To
detect this acid, therefore, in mixtures of the kind under con-
sideration, advantage is to be taken of its volatility. About
100 grams of the material is to be acidified with acetic acid,
introduced into a flask or retort connected to a condenser, and
then subjected to slow distillation until one-fifth of the liquid
part of the substance has collected in the receiver. Hydro-
cyanic acid, if present, will be found in the distillate by either
of the tests given in previous paragraphs (§§282–284).

# CHAPTER V.

## SPECIAL PART.

### ANALYSIS OF POTABLE WATER.

**361.** The water of wells, springs and rivers always contains foreign matter in solution, derived partly from the air, partly from the rocks and soil and partly from animal or vegetable sources. These substances are usually present in a solution of such high dilution that for their detection the ordinary methods of analysis must be somewhat modified. In considering these special methods, no account will be taken of mineral waters, the consideration of which does not lie within the scope of this work, but only those constituents will be regarded which are likely to be met with in the natural waters used for culinary purposes.

*The constituents of potable waters.*

We have to consider: first, the normal constituents; second, the constituents which are due to contamination of some sort.

**362.** The *normal constituents* of potable water which are most commonly met with are the following:

*Saline impurites in well-water.*

*a.* The carbonates, chlorides, and sulphates of calcium, magnesium and, in smaller amounts, of sodium and, more rarely, potassium.

*b.* Ferrous and ferric salts of the acids named are often present in small quantities, and also traces of aluminium compounds and of silicic acid.[1]

---

[1] Water containing alumina and silicic acid is usually turbid, from clay in suspension. Water containing iron salts becomes turbid upon standing and deposits a reddish or yellowish sediment.

c.  Minute traces of organic matter  .  .  .  .  *frequent.*
"        "        ammonium salts   .  .  .  *occasional.*
"        "        nitrates  .  .  .  .  .  .  "
"        "        nitrites  .  .  .  .  .  .  "

Any substances, other than those named, which may be found in spring or river water can be regarded as *abnormal* and as constituting a contamination.  The bodies enumerated under c are often due to contamination, and always so when found in comparatively large quantities.  (Compare §378). The commonest abnormal constituents are the following: <sub>Contamination.</sub>

d.  Lead, copper and other metals, derived from pipes, pumps or similar sources.

e.  Tarry or oily, or other odoriferous matters from factory refuse, etc.

f.  Large quantities of chlorides are often but not always derived from sewage.  Anything more than minute traces of the substances mentioned under "c" are probably due to contamination with animal refuse.  If much organic matter is present, without nitrogen compounds, it is usually due to decaying vegetable remains, such as leaves, sawdust, peat, etc., etc.

g.  Phosphates, derived from sewage.

**363.**  The hardness of water, that is, its power of curdling soap solution, is due to the calcium and magnesium salts which it contains.  The carbonates of calcium and magnesium which are found in solution are not the normal carbonates $CaCO_3$ and $MgCO_3$, but are the unstable, acid carbonates, often called bicarbonates, $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. The latter compounds are decomposed when the solution containing them is boiled, the normal carbonates of calcium and magnesium being precipitated. <sub>Hardness of water.</sub>

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$
$$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO_2$$

We find, accordingly, that water containing the carbonates and bicarbonates of calcium and magnesium becomes softer when boiled, in consequence of the removal of these salts from solution.

The sulphates and chlorides of calcium and magnesium are not altered by boiling, but remain in solution. We therefore **Permanent and temporary hardness.** distinguish the *temporary hardness* of water, which is due to carbonates and which is removed by boiling, from the *permanent hardness*, which is due to the sulphates[1] of calcium and magnesium and is not affected by boiling.

**364.** Those of the normal constituents, which are present in larger quantity, may be detected in the water directly. Those which are present in small amount are to be tested for after the water is concentrated by boiling.

Always note carefully in observing each reaction whether it is strongly marked, indicating an abundance of the body tested for; or whether it is barely perceptible, indicating a trace merely.

By testing both before and after concentration, a general idea of the abundance of certain constituents may often be formed.

### EXAMINATION OF THE WATER WITHOUT PREVIOUS CONCENTRATION.

**365.** Take for each test 50 c.c. of water.

**Chlorides.**    *a.* Acidify with nitric acid and add silver nitrate; a curdy precipitate indicates *chlorides.*

**Sulphates.**    *b.* Acidify with acetic acid and add barium chloride; a white precipitate indicates *sulphates.*

**Lime.**    *c.* Add about 1 gram of ammonium chloride, then, when this is dissolved, 10 c.c. ammonium oxalate solution; a white precipitate indicates *calcium.*

If a precipitate forms, digest in a warm place for at least five hours and filter.

**Magnesia.**    *d.* To the filtrate add sodium phosphate, then 20 c.c. concentrated ammonia; a crystalline precipitate, forming at once or after standing several hours, indicates *magnesium.*

**Iron.**    *e.* Acidify with hydrochloric acid: add a drop of potassium ferricyanide solution. A blue coloration indicates a *ferrous*

---

[1] Or chlorides.

and magnesium are
ion. We therefore
er, which is due to
g, from the *perma-*
ates[1] of calcium and

ts, which are present
the water directly.
are to be tested for

h reaction whether it
ce of the body tested
e, indicating a trace

ncentration, a general
tituents may often be

THOUT PREVIOUS

water.
ilver nitrate; a curdy

d barium chloride; a

n chloride, then, when
ate solution; a white

rm place for at least

hate, then 20 c.c. con-
pitate, forming at once
magnesium.

d a drop of potassium
on indicates a *ferrous*

---

*salt;* none appears, add a drop of potassium ferrocyanide Iron.
solution, when the mixture will turn blue, if a *ferric salt* is
present.

*f.* Add 2 c.c. of Nessler's reagent[1] (§40); a yellowish or Ammonia.
brownish color shows the presence of *ammonia.*

*g.* Acidify with hydrochloric acid and add a drop of potas- Nitrites.
sium iodide solution and 1 c.c. of starch paste (§§244, 245).
A blue color appearing within ten minutes indicates the
presence of *nitrites.*

This test is useless in the presence of ferric salts, which give
a similar indication.

In case iron has been found, apply Zambelli's test (§374) to
another portion of the water.

*h. Organic matter* may sometimes be detected by the odor
which is evolved when a sample of the water is boiled, either
alone or mixed with pure milk of lime (*i. e.* calcium hydrate
suspended in water).

More positive tests are given in §§375–377.

EXAMINATION OF THE WATER AFTER CONCENTRATION.

**366.** Add acetic acid in slight excess to one litre of the
water. Evaporate in a porcelain dish to one-tenth the original Fe, Al,
volume. If much calcium sulphate was present, a part of it and
may crystallize out during the evaporation. Filter, if neces- $SiO_2$.
sary. Test the precipitate for iron (§97), aluminium (§§64,
335), silica (§§228, 232).

Divide the filtrate into several parts. These parts are to be
used for any of the tests, *a, b, c, d, e,* of §365, which gave
negative results with the unconcentrated water.

DETECTION OF NITRATES.

**367.** Test 10 c.c. of the filtrate (preceding paragraph)
for nitrates, as follows. Mix with 10 c.c. of concentrated sul- Indigo
phuric acid and add to the mixture, while hot, a drop of indigo test for
solution.[1] If this turns yellow or colorless, nitrates (or nitrates.

---

[1] See List of Reagents, Table IV.
[1] Enough indigo should be added to the mixture to impart a very pale, but
distinct, blue to the same volume of distilled water.

**Nitrates.** nitrites) are present, but if the mixture remains blue, nitrates are not present in notable quantities.

If nitrites are present (§365, $g$), they must be removed before testing for nitrates. To accomplish this, mix, with the concentrated sample of water, one-half gram of ammonium chloride and evaporate to dryness on a water bath. This decomposes the nitrites, but not the nitrates.

$$NaNO_2 + NH_4Cl = NaCl = 2H_2O + N_2$$
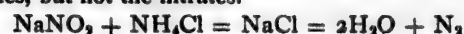
The residue is to be tested for nitrates as described above (or below).

**368.** Mix 10 c.c. of the filtrate with 20 c.c. of concentrated sulphuric acid. After cooling, add a minute fragment of diphenylamine. If the mixture turns blue, nitrates are present. This reaction is much more sensitive than the preceding.

### DETECTION OF LEAD AND COPPER.

**Cu and Pb.** **369.** If lead or copper are suspected they may be tested for, in 50 c.c. of the filtrate (§366), with hydrogen sulphide (§§130, 137). If a black precipitate forms, dissolve it in a little concentrated nitric acid, drive off most of the excess of acid by the application of heat and test one portion of the solution for lead (§134), another for copper (§140).

### DETECTION OF PHOSPHATES.

**H₃PO₄.** **370.** To another portion of the filtrate add a little nitric acid and evaporate to dryness. Treat the residue with a small quantity of water, filter, and test for phosphoric acid with ammonium molybdate (§212).

Instead of examining a concentrated sample of the water for phosphates, they may advantageously be detected by the following process.

To one litre of the water add 1 c.c. of ferric chloride and 1 c.c. of sodium acetate solution. Boil for five minutes and allow the precipitate to subside. Decant the clear portion and **Precipitation of FePO₄.** filter the remainder. Dissolve the precipitate in a small quantity of dilute nitric acid and test with ammonium molybdate for phosphoric acid (*l. c.*).

emains blue, nitrates

st be removed before

mix, with the concen-

ammonium chloride

. This decomposes

$2H_2O + N_2$

as described above

th 20 c.c. of concen-

d a minute fragment

rns blue, nitrates are

ensitive than the pre-

COPPER.

ed they may be tested

ith hydrogen sulphide

forms, dissolve it in a

most of the excess of

test one portion of the

opper (§140).

ATES.

ltrate add a little nitric

eat the residue with a

est for phosphoric acid

d sample of the water

sly be detected by the

. of ferric chloride and

oil for five minutes and

nt the clear portion and

cipitate in a small quan-

ammonium molybdate

### DETECTION OF SODIUM AND POTASSIUM.

**371.** Concentrate one litre of water in a porcelain vessel to about one-tenth its volume. Add enough barium hydrate[1] to make the reaction distinctly alkaline to turmeric paper. Boil, filter and evaporate the filtrate in a platinum or porcelain dish to the volume of about 5 c.c. and filter. To the filtrate add 1 c.c. ammonium oxalate solution, then boil and filter. Evaporate the filtrate to dryness; heat the residue to dull *K and Na.* redness; after cooling, dissolve in 5 c.c. hydrochloric acid and filter. The filtrate may be tested for sodium and potassium by the flame reaction or it may be mixed with platinum chloride and the mixture allowed to evaporate on a watch glass *in a place free from ammonia fumes.* If sodium and potassium are present, their chloroplatinates will appear in crystals of characteristic form (§33).[3]

### DETECTION OF AMMONIUM.

**372.** Solutions of ammonium salts when treated with Nessler's reagent[3] (§40) give a brownish precipitate, or, if the *Nessler's* solution is very dilute and free from salts of calcium and mag- *test for* nesium, a yellowish or brownish coloration. *NH₃.*

This test may be applied to the original water or, when the amount of ammonium present is exceedingly minute, to a sample in which the ammonia has been concentrated by distillation, as follows:

Introduce half a litre of the water into a flask attached to a *Testing* condenser and render it strongly alkaline with a solution of *the* sodium hydrate which has been boiled to free it from ammo- *distillate.* nia. Distill the mixture until 50 c.c. has distilled over. To

---

[1] This reagent must be free from the alkalies. After boiling with an excess of ammonium carbonate and subsequent filtration, the filtrate must leave *no residue* when evaporated to dryness.

[2] Not infrequently, the amount of sodium and potassium salts present may be too small to detect in one litre of water. In such cases a larger amount, such as five litres, can be employed. A similar remark applies equally to the detection of phosphoric acid. Usually, however, it is not worth while to examine larger amounts than one litre for a single test, except in connection with a quantitative analysis.

[3] *Vide* Table IV.

the distillate add 2 c.c. of Nessler's reagent, when the presence of ammonia will be indicated by a brownish coloration. An approximate judgement of the amount of ammonia can be formed from the depth of the color produced.

### DETECTION OF NITRITES.

**373.** If no nitrates were detected before concentration (§365, *g*), take 500 c.c. of the water and add enough pure milk of lime to render it alkaline to turmeric paper. Boil it down rapidly in a porcelain dish to about one-tenth its original volume and filter it. Test the filtrate for nitrites according to §365, *g*, or the following section. It will be free from iron, unless organic matter was present.

Zambelli's test for nitrites.

**374.** The most delicate reaction for nitrites is the following, which is known as Zambelli's test. To 50 c.c. of the water[1] add 5 c.c. of a saturated solution of sulphanilic acid, $C_6H_4NH_2SO_3H$, and 5 c.c. of dilute sulphuric acid. Allow the mixture to stand for ten minutes, then add 2 drops of a saturated solution of phenol ("carbolic acid") in water. Add ammonia to alkaline reaction. The appearance of a yellow color indicates a nitrite. This test will show the presence of 1 part of nitrite in 100,000,000 parts of water.

### ORGANIC MATTER.

Odor of residue.

**375.** Organic matter may sometimes be detected by the odor which is evolved, when the residue left by the evaporation of a litre of water, is heated, and by the charring of this residue.

**376.** The decolorizing of an acidified solution of potassium permanganate by organic matter may be used as a test for the latter.

Permanganate test.

Add 25 c.c. dilute sulphuric acid to 200 c.c. of the water and then add enough dilute potassium permanganate solution to color the whole pale violet. From 1 to 5 drops of the permanganate will usually be sufficient. Heat the whole to boil-

---

[1] The original water may be used, or a sample which has been boiled down according to the directions of §373.

ing. If it retains its color, organic matter is absent, but present if it is quickly made colorless.

**377.** Many kinds of organic matter, especially those which are found in contamination of excrementitious origin, are indicated with great delicacy by Griess's test. To 50 c.c. of water add a minute quantity of benzolsulphodiazid, and make the solution alkaline with *pure*[1] ammonia or sodium hydrate. A yellow coloration appears if organic matter of the kind referred to above is present.

*Griess's test for organic contamination.*

### INTERPRETATION OF THE RESULTS OF QUALITATIVE ANALYSIS OF WATER.

**378.** It is impossible, in many cases, to conclude definitively from the results of a qualitative analysis alone whether a given sample of water is fit for drinking purposes or not. Nevertheless, valuable indications are often obtained. Water which contains much organic matter or which has a distinct odor is not a suitable article of food, and should always be rejected without regard to further results of analysis. Such water favours the reproduction and development of micro-organisms which may be more or less noxious. Water contaminated with organic matter, more especially if this be of animal origin, when kept, undergoes a change, through the vital processes of organisms of a low order, by which the organic substances are, in part, converted into ammonia, nitrites or nitrates. If therefore more than slight traces of the last named compounds are found, this may be taken as an indication that the water had at a former period been contaminated with organic matter. Such water should be condemned, because germs of the micro-organisms above mentioned may remain after the decomposition of the original organic matter.

*Decomposition of the organic matter.*

When the putrefactive changes are continued for a long time, nitrates only may be found, with or without nitrites or ammonia.

---

[1] It is absolutely necessary to test the purity of the reagents by mixing them with 50 c.c. of distilled water. The mixture will remain colorless if they are free from organic impurity.

**Rain-water.** Rain-water collected from roofs and stored in cisterns is often rich in organic matter derived from dust, leaves, etc., on the roof. The pollen from numerous kinds of trees is a prolific source of organic contamination of the cistern water in some localities. The *absence* of anything more than mere traces of *chlorides* from waters such as this distinguishes them at once from those which have been contaminated by sewage or through underground leakage from cesspools, although the abundant nitrogen compounds sometimes found in the former might lead to the presence of animal refuse being suspected.

**Sewage.** If the quantity of chlorides is considerable and if, at the same time, distinct reactions are obtained for nitrites, ammonia or organic matter, the water is to be unhesitatingly condemned, on the ground that it is probably contaminated with sewage or animal *excreta* in some form, since the latter contain sodium chloride in abundance and also nitrogen compounds. In cases of suspected sewage contamination, Griess' test (§377) is very valuable. But if it fails to give any positive indication, the water is not therefore necessarily safe, because, as already explained, the germs of disease may remain after the original organic contamination is destroyed by decomposition into ammonia, etc.

**Boiler scale.** Water containing much calcium and magnesium, that is, water which is very *hard*, is not necessarily unwholesome, but is unsuitable for mechanical purposes. Such water, when used to supply steam boilers, produces an incrustation or *scale* which interferes with the development of steam and greatly shortens the life of the boiler.

The composition of the scale depends upon that of the water. It often consists of calcium and magnesium carbonates mixed with calcium sulphate and magnesium hydrate.

Water containing much magnesium sulphate (or chloride) frequently corrodes the boiler plates quite rapidly, in consequence of the formation of free acid and basic salts.

$$MgCl_2 + H_2O = MgClOH + HCl$$
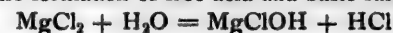
## ANALYSIS OF ALLOYS.
### PRELIMINARY EXAMINATION.

**379.** Heat on charcoal before the blowpipe (§13). Arsenic, antimony, zinc, lead, bismuth, and sometimes tin and silver may be detected by their reactions as described in the directions given under the headings of those metals. *(Arsenic, etcetera.)*

**380.** Heat in a matrass (§14). Mercury is indicated by a gray sublimate. Cadmium and arsenic may also form sublimates which can be easily distinguished from that of mercury. (§§127, 166).

A fuller outline scheme for the blowpipe examination of alloys is given in Table I (p.104).

### SOLUTION.

**381.** Gold and platinum are not attacked by nitric acid. Antimony and tin are oxidized by nitric acid, but the resulting oxide of the former is nearly and that of the latter quite insoluble in both water and nitric acid. *(Action of $HNO_3$ on alloys.)*

Aluminium and some of its alloys, distinguishable by a low specific gravity, are scarcely attacked by nitric acid. Hydrochloric acid is the best solvent for aluminium and the alloys referred to.

All other metals are oxidized by nitric acid, the resulting oxides being converted into nitrates which dissolve.

**382.** Warm the substance with a mixture of nitric acid and water in equal parts. If the alloy completely dissolves, either at once or after the addition of more water, gold, platinum and tin are absent, and only traces of antimony can be present. Proceed with the solution according to the general scheme (§324, *et seq.*), first removing most of the nitric acid, if it is present in great excess, by evaporation *nearly* to dryness and subsequent dilution. If a precipitate is thrown down when the solution is diluted, bismuth is probably present (§147). In this case, filter, wash the precipitate and then boil it with sodium hydrate and stannous chloride. If it turns black (*v.* §152) the presence of bismuth is confirmed. *(Solution in $HNO_3$.)*

For the detection of the metals in the solution, pass to §324.

**383.** If a residue is left, insoluble in nitric acid and water, it may consist of gold, platinum, metastannic acid or metantimonic acid.

Au and Pt.   If it is metallic, dissolve it in *aqua regia* (four parts of concentrated hydrochloric to one of nitric acid) and test the solution for gold and platinum (§§183, 186).

Sb, Sn and As.   If the residue is a white powder, tin or antimony is indicated, and the precipitate may also contain arsenic acid. Test the residue for antimony, tin and arsenic according to §§164, 170, 179, 180, and for bismuth (§152).

**384.** The insoluble residue may with advantage be examined in the following way after washing and drying.

Blowpipe examination of the residue.   Heat one portion in a matrass (§14) with a little *dry* potassium cyanide. An arsenical mirror will appear if this metal is present. If it does so, cut off the lower end of the tube and cautiously heat the mirror so as to oxidize it. If it be arsenic, it will form the characteristic crystalline film of colorless octahedrons, distinctly visible under the microscope.

Heat another portion on charcoal in the oxidizing flame. Arsenic will be driven off and antimony will form a film which will turn greenish when heated with cobalt solution. If antimony is absent, the non-volatile residue consists of $SnO_2$, which may be reduced to tin with the cyanide flux, §165.

**385.** If the alloy partially dissolves in the nitric acid but also leaves an insoluble residue, examine the latter according to the preceding paragraph and analyze the solution according to the general scheme (§324).

Partial solution.

# ATOMIC WEIGHTS AND QUANTIVALENCE OF THE ELEMENTS.

The atomic weights are given in accordance with Meyer and Seubert's calculations, excepting in cases where more recent determinations have made changes necessary. There is so much that is hypothetical and arbitrary in the conception of quantivalence, that the numbers representing this atomic attribute are, unlike those expressing atomic weights, to be taken with reserve as presenting theory, in many cases at least, rather than as final statements of fact.

| Name. | Symbol. | Quantivalence. | Atomic Weight. | Name. | Symbol. | Quantivalence. | Atomic Weight. |
|---|---|---|---|---|---|---|---|
| Hydrogen | H | I | I | Molybdenum | Mo | IV, VI | 95.9 |
| Aluminium | Al | III | 27.04 | Nickel | Ni | II, III | 58.56 |
| Antimony | Sb | III, V | 119.6 | Niobium[2] | Nb | III, V | 93.7 |
| Arsenic | As | III, V | 74.9 | Nitrogen | N | III, V | 14.01 |
| Barium | Ba | II | 136.86 | Osmium | Os | II, IV, VI, VIII | 191.2 |
| Beryllium | Be | III | 9.03 | Oxygen | O | II | 15.96 |
| Bismuth | Bi | III, V | 207.5 | Palladium | Pd | III, IV, VI | 106.2 |
| Boron | B | III, V(?) | 10.9 | Phosphorus | P | III, V | 30.96 |
| Bromine | Br | I, VII [1] | 79.76 | Platinum | Pt | II, IV, VI, VIII | 194.34 |
| Cadmium | Cd | II | 111.7 | Potassium | K | I | 39.03 |
| Cæsium | Cs | I | 132.7 | Rhodium | Rh | II, IV, VI | 104.1 |
| Calcium | Ca | II | 39.91 | Rubidium | Rb | I | 85.2 |
| Carbon | C | II, IV | 11.97 | Ruthenium | Ru | III—VII | 103.5 |
| Cerium | Ce | III, IV | 139.87 | Samarium | Sm | (?) | 150(?) |
| Chlorine | Cl | I, VII [1] | 35.37 | Scandium | Sc | III | 43.97 |
| Chromium | Cr | III, VI | 52.45 | Selenium | Se | II, IV, VI | 78.97 |
| Cobalt | Co | II, III | 58.74 | Silicon | Si | IV | 28.33 |
| Copper | Cu | II, I | 63.33 | Silver | Ag | I | 107.66 |
| Didymium | Di | IV | 145. | Sodium | Na | I | 23.00 |
| Erbium | E | II | 166. | Strontium | Sr | II | 87.3 |
| Fluorine | F | I, VII | 19.06 | Sulphur | S | II, IV, VI | 31.98 |
| Gallium | Ga | IV | 69.9 | Tantalum | Ta | V | 182. |
| Germanium | Ge | IV | 72.31 | Tellurium[3] | Te | II, IV, VI | 126.7 |
| Gold | Au | I, III | 196.85 | Thallium | Tl | I, III | 203.7 |
| Indium | In | III | 113.4 | Thorium | Th | IV | 232. |
| Iodine | I | I, VII [1] | 126.54 | Tin | Sn | II, IV | 118.8 |
| Iridium | Ir | II, IV, VI | 192.5 | Titanium | Ti | II, IV | 48.01 |
| Iron | Fe | II, III | 55.88 | Tungsten | T | III, IV, VI | 193.6 |
| Lanthanum | La | IV | 138.5 | Uranium | U | VI, IV | 238.9 |
| Lead | Pb | II, IV | 206.39 | Vanadium | V | III, V | 51.1 |
| Lithium | Li | I | 7.01 | Ytterbium | Yt | | 172.6 |
| Magnesium | Mg | II | 23.94 | Yttrium | Y | IV | 89.6 |
| Manganese | Mn | II, IV, VI, VIII | 54.8 | Zinc | Zn | II | 65.2 |
| Mercury | Hg | II, I | 199.8 | Zirconium | Zr | IV | 90.4 |

[1] Probably also III and V.

[2] Also called Columbium, Cb.

[3] According to the latest researches, the atomic weight of tellurium is in doubt.

# TABLE I.
## BLOWPIPE REACTIONS OF SINGLE METALS AND ALLOYS.

| -----Heat on Charcoal in the Oxidizing Flame:----- | | |
|---|---|---|
| **1.** *A white incrustation is formed.* | *Flame coloration.* | *The coating moistened with Co. Sol. and ignited in O.F. becomes* |
| ALUMINIUM: Al — White coating on and near assay, not volatile in O.F. or R.F., infusible. | White. | Sky-blue. |
| TIN: Sn — Coating on and near the assay pale yellow when hot, white when cold. Not volatile in O. F. or R. F. | None. | Tea-green. |
| ZINC: Zn — Coating in the charcoal yellow when hot, whitish when cold. Volatile in R. F. | Greenish white. | Yellowish green. |
| MAGNESIUM: Mg — White coating, hot and cold. Not volatile. | White. | Flesh-colored. |
| ANTIMONY: Sb — White coating on charcoal. Volatile in R.F., less so in O.F. No odor. | Pale green. | Dull dark green. |
| ARSENIC: As — White coating far from the assay. Highly volatile in O. F. Alliaceous odor. | Pale blue. | Heated in open tube gives white glistening sublimate of octahedral crystals. |
| MERCURY: Hg — Volatile without coating or odor. | None. | Heated in a matrass gives a mouse-gray film. (§127.) |

| **2.** *A colored incrustation is formed on the Ch.* | | *Heated on Ch. with sulphur & KI a coating is formed which is* |
|---|---|---|
| LEAD: Pb — Coating is dark yellow when hot, sulphur yellow cold. Fusible. Coating gives *azure blue* to R. F. | Azure blue. | Bright yellow. |
| BISMUTH: Bi — Coating is deep orange when hot, lemon yellow cold. Volatile. Coating imparts no color to R. F. | None | Red, orange, and yellow. |
| SILVER: Ag — Dark red coating slowly forms near assay, which remains bright. | Pale violet. | |

| **3.** *Assay oxidizes without incrusting charcoal.* | *Borax Bead in O. F.* | *Borax Bead in R. F.* | *Soda Bead in O. F.* |
|---|---|---|---|
| COPPER: Cu — Assay fuses and turns black in O. F., then in R. F. becomes red. Colors the flame *green*, moistened with HCl colors flame *sky-blue* | Hot, green. Cold, blue. | Red and opaque. | Hot, green. Cold, white and opaque. |
| NICKEL: Ni — Assay does not fuse, turns blue-black in O. F., gray in R. F. Magnetic. | Hot, violet. Cold, brown. | Gray to colorless. | Insoluble. |
| COBALT: Co — Like nickel. | Blue. | Blue. | Hot, pale red. Cold, gray. |
| IRON: Fe — Assay turns black in O. F., same in R. F. The oxide is magnetic. | Hot, violet to black Cold, violet to amethyst. | Bottle-green. | Insoluble. |
| MANGANESE: Mn — Assay turns reddish brown in O. F. and then does not change in R. F. Infusible | Hot, yellow to red Cold, yellowish green. | Colorless. | Deep grass-green. |
| CHROMIUM: Cr — Assay turns dark green in O. F. and then does not change in R. F. Infusible. | Hot, yellow to red Cold, colorless to yellow. | Hot, green. Cold, green. | Hot, brownish yellow. Cold, lemon - yellow. |

| **4.** *Assay does not oxidize nor form coating.* | *Abbreviations:* |
|---|---|
| GOLD: Au — Assay fuses, otherwise no change. | Ch., Charcoal. |
| PLATINUM: Pt — Infusible, no change. | O. F., Oxidizing flame. |
| MERCURY: Hg — Volatilizes. (See above.) | R. F., Reducing flame. |
| | Co. Sol., Cobalt nitrate solution. |

## TABLE II.

### SUMMARY OF EXAMINATION OF NON-METALLIC SOLIDS BY THE BLOWPIPE.

**1.** Heat the Assay-piece alone on Charcoal in the Oxidizing Flame.

If a coating is formed, it may be the oxide of:— As, Sb, (Zn), Pb, Bi, Cd, (Compare Table I, 1 and 2) or it may be a compound of NH₄ or Hg or K or Na.

If deflagration occurs, it is probably due to a *Chlorate* or a *Nitrate*, but possibly to an oxide of *Mercury, Silver* or *Gold*.

If the assay is white after ignition and infusible, test in the O. F. with Co. Sol.
The color may show:— $Al_2O_3$, $SnO_2$, $ZnO$, $MgO$, $Sb_2O_4$, (Compare Table I, 2.) $SiO_2$ pale blue (see §357).

If metallic globules form, they consist of *Silver* or *Gold*.

If a gray, spongy, infusible metal is reduced, this is *Platinum*

**2.** Mix the assay with "cyanide flux" (3 parts $Na_2CO_3$ 2 parts KCy, 1 part borax) and fuse on Ch. in the R. F.

If a coating is formed it may be the oxide of:— As, Sb, Zn, Pb, Bi, Cd. (Compare I.)

Soak residue after removal from Ch. in water. If metal is reduced it may be Sb, Sn, Bi, Fe, Pb, Cu, Ni, Co, Ag, Au, Pt. Separate the metal and examine according to Table I.

**3.** Moisten the assay with $H_2SO_4$, dip a fine platinum wire in it and observe the color imparted to the flame directly, and as seen through blue glass and green glass.

| | | |
| --- | --- | --- |
| Yellowish green, | . . . Ba | Yellow, . . . Na |
| Emerald green, | $H_3BO_3$ | Crimson, . . . Li, Sr |
| Green (blue when HCl is added), | . . . Cu | Violet, . . . K |
| Orange, | . . . Ca | Azure blue, . . . Pb |
| | | Faint greenish, . . . Sb |
| | | Faint blue, . . . As |

**4.** Test with borax bead in O. F. and R. F.
The bead will be colored by:— Cu, Ni, Co, Fe, Mn, Cr. (Compare with Table I, 3.)

**5.** Fuse on Pt foil with "oxidizing flux" ($Na_2CO_3$ four parts, $KNO_3$ one part). Observe color when cold.
Grass green, shows Mn ... Lemon yellow, shows Cr

**6.** Heat a copper wire in O. F., then dip it into the substance and hold it again in the flame.
Flame is blue, *Chlorine.* / Flame is greenish blue *Bromine.* (not certain.)

**5 a.** Transfer the mass to Ch. and fuse in R. F., then transfer to silver coin and moisten. Silver turns black, shows a *sulphur* compound.

**7.** Heat with $K_2S_2O_7$ in a matrass. Violet vapours and black sublimate, *Iodine.*

**8.** Fuse in a matrass with dry $Na_2CO_3$ and magnesium. (§214).
The mass when crushed and moistened smells of $PH_3$. *Phosphate.* / Glass is etched, *Fluoride.*

## TABLE III.
### SOLUBILITIES OF SALTS AND BASES.

(For explanation of signs see page 110)

| ACID GROUP. | NAME AND SYMBOL | FIRST GROUP | | | SECOND GROUP | | | | THIRD GROUP | | | | FOURTH GROUP | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Ammonium NH₄ | Potassium K | Sodium Na | Calcium Ca | Barium Ba | Magnesium Mg | Strontium Sr | Aluminium Al | Chromium Cr | Iron Fe^d | Iron Fe^m | Manganese Mn | Zinc Zn | Cobalt Co | Nickel Ni |
| | Hydrates, ROH | | S | S | P S— | S C | P S— | S | P A / S—+ | P A / S— | P A / S— | P A / S— | P A / S— & am. | P A / s—+ & am. | P A / S— | P A / S— & am. |
| I { | Sulphates, R₂SO₄ | S C | S C | S C | P C | P C / +— | S C | P C / +— | S | S / green | S C / green-ish | P | S C / pink | S C | S C / rose | S C / green |
| | Carbonates, R₂CO₃ | S C | S C | S C | P S— | P S— | P S / am. cl. | P S— | P dec. | P dec. | P dec. | P dec. | P / pink | P A | P / blue | P / green |
| | Fluorides, RF | S C | S C | S C | P | P | P | P | S [1] | S [2] | P | P | P S— | P | P S— | P S— |
| II,1 { | Oxalates, R₂C₂O₄ | S C | S C | S C | P C / S— | g C / S— | P S / s—& am. cl. | P C / S— | S | S / violet | P C / s— yellow | P | P C | P C | P C / pink | P C |
| | Sulphites, R₂SO₃ | S C | S C | S C | S | P C / S— | S C | P C / S— | S | S | S | S / red | S | S | S | S |
| | Arsenates, R₂HAsO₄ R₃AsO₄ | P C | S | S C | P S— | P S— [6] | P S— | P S— | P A / S— | P S— | P A / S— | P S— | P A / S— | P A / s—+ | P A / s—+ am. cl. | P A / s—+ am. cl. |
| | Borates, R₂O(B₂O₃)x | S | S | S | P S— / & am. cl. | P S— | P S— | P S— / & am. cl. | P A / S— | P S— | P dec. | P S— | P S— | P S— | P S— | P S— / and am. cl. |
| II,2 { | Chromates, R₂CrO₄ | S C | S C | S C | S | P S— [4] | P S— [3] / S C | P S— [3] | P / s—+ | P / s—+ | P S— | P S— | S | S | | S C |
| | Phosphates, R₂HPO₄ R₃PO₄ | S C | S C | S C | P A / S— | P A / S— | P A / S— | P A / S— | P A [s] / S— | P A [s] / S— | P A [s] / S— | P A / S— | P A / S— | P A / s—+ | P A / S— | P A / S— |
| | Silicates, | S C | S | S | P A / S— | P A / S— | P A / S— | P A / S— | P A / S— | P A / S— | P A / S— | P A / S— | P A / S— | | P A / S— | P A / S— |

| Group | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **II,2** | ARSENATES, $R_3HAsO_4$, $R_3AsO_4$ | P C | S | SC | PS— & am.cl | PS— | PS—[6] | PS— | PA S— | PS— | PS— | PS— | PA S— | PS— | PS— | S— | S—+ | am.d PS— am.d |
| | BORATES, $R_2O(B_2O_3)x$ | S | S | S | PS— & am.cl | PS— | PS— | PS— | SA S— | PS— | PS— & am.cl | PS— | PS— | PS— | PS— | PS— | PS— | PS— and am.d |
| | CHROMATES, $R_2CrO_4$ | SC | SC | SC | S | PS—[4] | PS—[3] SC | PS—[3] | P S—+ | P S— | PA S— | P S— | PS— | PS— | PA S— | S | S | S C |
| | PHOSPHATES, $R_2HPO_4$, $R_3PO_4$ | SC | SC | SC | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— |
| | SILICATES, R...SIO... | S | S | S | PA S— | PA S— | PA S— | PA | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— | PA S— |
| **III,1** | FERRICYANIDES, $R_3FeCy_6$ | SC | SC red | S | PS— | PS— | PS— | PS— | S | PA S— | P— blue | S brown | P— | PS— | P— | PS— | P— | P— |
| | FERROCYANIDES, $R_4FeCy_6$ | SC yellow | SC yellow | S | PS— | PS— | PS— | PS— | S | S | P— | P— blue | PS— | PS— | P— | P— | P— | P— |
| | SULPHOCYANATES, RSCN | SC | SC | SC | SC | SC | SC | SC | SC | SC | S | S red | S | S | S blue | S | S |
| **III,2** | CHLORITES, $RClO_2$ | S | S | S | S | S | S | S | S | S | | | | | | | |
| | HYPOCHLORITES, RClO | S | S. | S | S | S | S | S | S | S | S | | S | S | | | |
| | NITRITES, $RNO_2$ | | S | S | S | S | S | S | S | S | S | | S | | | | |
| **III,3** | SULPHIDES, $R_2S$ | S | S | S | PS— & am.cl | S | PS— am.cl | S | S | PS— black | PS— pink | PS—[s] white | PS—[s] white | P black | P black | | |
| | THIOSULPHATES, $R_2S_2O_3$ | S | S | S | S | S | S | S | S | S | S | S | S | S | S | | |
| **III,4** | BROMIDES, RBr | SC | SC | SC | SC | SC | SC | SC | S | SC green | SC red | SC pink | SC | SC | SC red | SC green |
| | CHLORIDES, RCl | SC | SC | S | S | SC | SC | SC | S | SC green | SC orange | SC pink | SC | SC | SC red | SC green |
| | CYANIDES, RCN | S | S | PS— | PS— | S | PA S— | PA S— | PA &S | PA S in exces | PA S—+ | P A | PA S in am. |
| | IODIDES, RI | SC | SC | SC | SC | S | S | S green | SC dec. brown | SC pink | SC | SC red | SC green |
| **IV** | TARTRATES, $R_2C_4H_4O_6$ | SC[7] | SC[7] | S | PS— & am.cl | P | P— & am.cl | S | S A | P | PS+ | S | PS—+ |
| **V** | ACETATES, CHLORATES, NITRATES | S | S | S | S | S | S | S | S | S | S | S | S |

TABLE III—*Continued.*

## SOLUBILITIES OF SALTS AND BASES.

(For explanation of signs, see page 110.)

108

| ACID GROUP | NAME AND SYMBOL | FIFTH GROUP | | | | | | SIXTH GROUP | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | BIS-MUTH, Bi | CAD-MIUM, Cd | COP-PER, Cu | LEAD, Pb | MERCU-ROUS, Hg^I | MER-CURIC, Hg^II | SIL-VER, Ag | ANTI-MONY, Sb | ARSE-NIC, As | GOLD, Au | PLATI-NUM, Pt | STAN-NOUS, Sn^II | STAN-NIC, Sn^IV |
| I | HYDRATES, ROH | P S — & am. cl | P S — & am. & am. cl | P S — & am. blue | p S — + | P S — & m.cl. black | §P S — am.dec orange | §P S — am.dec. brown | P S — + & am.cl | S | P S — + brown | P S — dec. brown | P S — + | P |
| | SULPHATES, R₂SO₄ | S dec. | S C | S C blue | P S + | p S — | dec.¹⁵ | p C | p S — | S | dec. | dec. | S | dec. |
| II,1 | CARBONATES, R₂CO₃ | P dec. | P S — | P S — dec. green | P S — dec. | P S — dec. gray | P S — dec. orange | S — & am. | | | dec. | dec. brown | P S + | dec. |
| | FLUORIDES, RF | S | p S — | P S — blue | P S — | P S — | p S — | S | S | S | | S yellow | S | P |
| | OXALATES, R₂C₂O₄ | P S — | P S — | P S — pale blue | P S — | P S — | P S — | P S — | P S — | P S — | dec. | | P | S |
| | SULPHITES, R₂SO₃ | P S — | p S — | P S — + pale blue | P S — | P | | P S — & am. | P | | dec. | | S | dec. |
| II,2 | ARSENATES, R₂HAsO₄ R₃AsO₄ | P S — | P S — | P S — green | P S — | P S — | P S — | P S — & am. | P S — | | | | P S — | P S — |
| | BORATES, R₂O(B₂O₃)x | P S — | p S — | P S — green | P S — | P S — | | p S — | | | | | P S — | |
| | CHROMATES, R₂CrO₄ | P S — brown | P S — yellow | S brown | P p — yellow | P S — vermilion | P p — garnet | P S — red | p S — | | | P | dec. | |
| | PHOSPHATES, R₂HPO₄ R₃PO₄ | P S — | P S — | P S — green | P S — | P S — | P S — | P S — & am. yellow | p — | | | | P S — | P S — |
| | SILICATES, R₂O(SiO₂)x | | P | P green | P | | | | | | | | | |

The solubilities of many of the salts enumerated in this Table are materially modified by the presence of other salts in the solution; the thiosulphates of copper or lead being, for example, readily soluble, in presence of sodium thiosulphate, which unites with them

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ARSENATES, $R_3HAsO_4$, $R_3AsO_4$ | P S — | P S — | P S — | P S — | P S — | P S — | P S — | | | p S — | P S — | P S — | P S — am. |
| BORATES, $R_2O(B_2O_3)x$ | P S — brown | P S — & am. | P S — green | P S — | P S — | | P S — | | | P S — | | dec. | P S — |
| II,₂ CHROMATES, $R_2CrO_4$ | P S — yellow | P S — & am. | S brown | P p — yellow | P S — vermilion | P p — garnet | P S — red | p S — | | P p — yellow | P | dec. | |
| PHOSPHATES, $R_4HPO_4$, $R_3PO_4$ | P S — | P S — | P S — green | P S — | P S — | P S — | P S — & am. yellow | P — | | P S — & am. yellow | | | P S — |
| SILICATES, $R_2O(SiO_2)x$ | P | P | P, green | P, green | | | | | | P S — & am. yellow | | | |
| III,₁ FERRICYANIDES, $R_6FeCy_6$ | P — A brown yellow | P S — & am. | P S am. dun | P S — | | | P — | | | P — | | P S — | P S — |
| FERROCYANIDES, $R_4FeCy_6$ | P — yellowish | P S — & am. | P — red | P S — | | | P — | | | P — | P — | P — | |
| SULPHOCYANATES, RSCN | ? | p S am. | p black | P | P — | P S — | P — | | P | p S — | P S — | S | S |
| CHLORITES, $RClO_2$ | | | | P dec. | | | P | | | P | | | |
| III,₂ HYPOCHLORITES, RClO | | | | S dec. | | | P dec. | | | P | S dec. | | |
| NITRITES, $RNO_2$ | | | S | S | P | P S — | P S am. | | | P S am. | S C | dec. | S dec. |
| III,₃ SULPHIDES, $R_2S$ | P — A brown | P — A yellow | P — A brown | P — A black | P | P — A black | P — A black dec. | P — A orange | P — A lemon | P — A brown | P — A brown | P — A brown | P — A yellow |
| THIOSULPHATES, $R_2S_2O_3$ | S | S | P | P | | S | P dec. | S | | S dec. | S dec. | S | S |
| BROMIDES, RBr | S dec. | S | S greenish blue | P — | P p | S | P — | S dec. | S | S orange | S brown | S | S dec. |
| III,₄ CHLORIDES, RCl | S dec. | S | S C blueish green | p C | P — A | S C | P — A S in am. | S dec. | S | S yellow | S orange | S | S dec. |
| CYANIDES, RCN | | | P S — | P S — | S | S | P S — | P | S C | S C | P — | | |
| IODIDES, RI | p | S | S dec. | p C yellow | P S — greenish | P S — red | P — yellow | p S — | S | dec. brown | S brown | S | S dec. |
| IV TARTRATES, $R_2C_4H_4O_6$ | dec. | P | P S — green | P S — + | P S — | P | P S am. | S | | dec. | S | P | |
| V ACETATES, CHLORATES, NITRATES | S | S | S green, blue | S C | S | S C | S | S | S | S | S | S | S |

TABLE III—*Continued.*

## EXPLANATION OF SIGNS AND REMARKS TO THE TABLE OF SOLUBILITIES.

(See pages 106–109).

### ABBREVIATIONS.

P.—Insoluble or nearly so — precipitated from highly dilute solutions.

p.—Slightly soluble — precipitated from concentrated solutions.

S.—Soluble.

C.—Crystalline.

am.—Ammonia.

am. cl.—Ammonium chloride.

dec.—Decomposes in contact with water.

—.—in dilute acids (HCl or $HNO_3$).

+.—in solutions of the alkalies.

EXAMPLES: — P S — +, a precipitate, soluble in dilute acids and alkalies: P p —, a precipitate, slightly soluble in acids, P C — +, a crystalline precipitate, insoluble in acids and alkalies.

---

### NOTES.

(The numbers refer to the Table).

*1.*—Double salts with NaF, KF, and $NH_4F$, are insoluble.

*2.*—Many double fluorides of Cr with other bases are insoluble.

*3.*—$SrCrO_4$ is soluble in chromic and other acids.

*4.*—Insoluble in chromic acid.

*5.*—Insoluble in acetic acid.

*6.*—Soluble in presence of ammonium chloride and of citrates.

*7.*—The acid tartrate is sparingly soluble.

*8.*—Soluble in presence of chlorides.

*9.*—Readily decomposes into cuprous sulphocyanate, which is colorless and insoluble in acids.

*10*—Soluble in hot concentrated hydrochloric acid.

*11.*—Soluble in hot concentrated nitric acid.

*12.*—Soluble only in aqua regia.

*13.*—The oxychloride, bismuthyl chloride, is insoluble in water, soluble in acids

*14.*—Mercurous acetate is sparingly soluble in water, soluble in acids.

*15.*—Becomes yellow on decomposition.

*TABLE IV.* III

## TABLE IV.

### LIST OF REAGENTS USED IN SOLUTION.

It is convenient, whenever practicable, to make up the solution of each reagent of such a strength that the number of grams of the reagent contained in one litre shall be a simple multiple of the molecular weight of the active constituent. The quantities given in the fourth column are, so far as possible, in accordance with this plan.

| Formula of Reagent. | Molecular Weight. | Name. | Number of Grams in 1 Litre of the Solution. |
|---|---|---|---|
| $H_2SO_4$ | 98 | Concentrated Sulphuric Acid | 1840 |
| $H_2SO_4$ | 98 | Dilute Sulphuric Acid | 196 |
| $HNO_3$ | 63 | Concentrated Nitric Acid | 1520 |
| $HNO_3$ | 63 | Ordinary Nitric Acid | 850 |
| $HNO_3$ | 63 | Dilute Nitric Acid | 126 |
| $CH_3COOH$ | 60 | Strong Acetic Acid | 300 |
| $CH_3COOH$ | 60 | Dilute Acetic Acid | 60 |
| HCl | 36.4 | Fuming Hydrochloric Acid | 500 |
| HCl | 36.4 | Concentrated Hydrochloric Acid | 364 |
| HCl | 36.4 | Dilute Hydrochloric Acid | 72.8 |
| $Cl_2 + Aq$ | 70.8 | Chlorine-water | Saturated |
| $Br_2 + Aq$ | 160 | Bromine-water | Saturated: ab't 30 |
| HCl } HNO₃ } | | Aqua Regia | 800 c.c. Conci. HCl 200 c.c. " HNO₃ |
| KOH | 65 | Potassium Hydrate | 650 |
| KOH | 65 | Dilute Potassium Hydrate | 130 |
| NaOH | 40 | Dilute Sodium Hydrate | 80 |
| $NH_3$ | 17 | Concentrated Ammonia | 340 |
| $NH_3$ | 17 | Dilute Ammonia | 34 |
| $Ba(OH)_2, 8H_2O$ | 315 | Barium Hydrate | 94.5 |
| $Ca(OH)_2$ | 56 | Calcium Hydrate | Saturated Solution |
| $(NH_4)_2S$ | 68 | Ammonium Sulphide | 68 |
| $(NH_4)_2S_x$ | | Yellow Ammonium Sulphide | About 100 |
| $Na_2HPO_4, 12H_2O$ | 358 | Sodium Phosphate | 179 |
| $(NH_4)_2C_2O_4, 2H_2O$ | 158 | Ammonium Oxalate | 31.6 |
| $NaC_2H_3O_2, 3H_2O$ | 136 | Sodium Acetate | 136 |
| $(NH_4)_2CO_3$ | 94 | Ammonium Carbonate | 94 |
| $KNO_2$ | 85 | Potassium Nitrite | 400 |
| $K_2Cr_2O_7$ | 300 | Potassium Pyrochromate[1] | 150 |

[1] Also called potassium dichromate.

*TABLE IV—Continued.*

| Formula of Reagent. | Molecular Weight. | Name. | Number of Grams in 1 Litre of the Solution. |
|---|---|---|---|
| $(NH_4)_2MoO_4$ $HNO_3$ | 196 | Ammonium Molybdate Solution | 75 255 c.c. *Con.* $HNO_3$ |
| $NH_4Cl$ | 52.4 | Ammonium Chloride | 105 |
| $K_4FeC_6N_6, 3H_2O$ | 456 | Potassium Ferrocyanide | 45.6 |
| $KSCN$ | 97 | Potassium Sulphocyanate | 97 |
| $BaCl_2, 2C_2O$ | 244 | Barium Chloride | 24.4 |
| $Ba(NO_3)_2$ | 261 | Barium Nitrate | 26.1 |
| $CaSO_4, 2H_2O$ | 172 | Calcium Sulphate | *Saturated: about* 2 |
| $CaCl_2$ | 111 | Calcium Chloride | 111 |
| $MgSO_4, 7H_2O$ | 246 | Magnesium Sulphate | 246 |
| $MgSO_4, 7H_2O$ $NH_4Cl$ | | Magnesia Mixture | { 123 105 |
| $FeSO_4, 7H_2O$ | 278 | Ferrous Sulphate | 278 |
| $FeCl_3, 6H_2O$ | 270 | Ferric Chloride | 270 |
| $Fe_2(SO_4)_3, 9H_2O$ | 562 | Ferric Sulphate | 281 |
| $AgNO_3$ | 169 | Silver Nitrate | 16.9 |
| $HgCl_2$ | 271 | Mercuric Chloride | 54.2 |
| $SnCl_2, 2H_2O$ | 226 | Stannous Chloride | *About* 113 |
| $PtCl_4, 8H_2O$ $H_2PtCl_4$ | 480 | Platinum Chloride, or Chloroplatinic Acid | 96 |
| $Co(NO_3)_2, 5H_2O$ | 272 | Cobaltous Nitrate | 27.2 |
| $KOH$ $KI$ $HgCl_2$ | | Nessler's Reagent [a] | { 150 62.5 *About* 31.2 |

[a] In preparing Nessler's reagent, the potassium iodide and the mercuric chloride are to be separately dissolved; the former in 100 c.c., the latter in about 800 c.c. of water, with the aid of heat. When cold, add the second solution to the first, with constant stirring, until a *permanent* precipitate begins to form, then add the potassium hydrate, and make up to 1 litre. After standing for some time, the clear portion of the solution is to be drawn off for use.

| | Number of Grams in 1 Litre of the Solution. |
| --- | --- |
| | 75 |
| | 255 c.c. *Com.* HNO₃ |
| | 105 |
| | 45.6 |
| | 97 |
| | 24.4 |
| | 26.1 |
| | *Saturated: about 2* |
| | 111 |
| | 246 |
| | { 123 |
| | { 105 |
| | 278 |
| | 270 |
| | 281 |
| | 16.9 |
| | 54.2 |
| | *About* 113 |
| | 96 |
| | 27.2 |
| | { 150 |
| | { 62.5 |
| | { *About* 31.2 |

... mercuric chloride are to be ... 800 c.c. of water, with the ... ith constant stirring, until a ... drate, and make up to 1 litre. ... n is to be drawn off for use.

# INDEX.

# ERRATA.

p. 25; fourth line from bottom, for "ammonium" *read* "sodium,"

p. 39; marginal note, last line, for "As₂O₃" *read* "Sb₂O₃."

p. 66; seventeenth line from bottom, *insert* after "card" the words, "with sodium carbonate."

113

TABLE IV—*Continued.*

| Formula of Reagent. | Molecular Weight. | Name. | Number of Grams in 1 Litre of the Solution. |
|---|---|---|---|
| (NH₄)₂MoO₄ } HNO₃ { | 196 | Ammonium Molybdate Solution | 75 255 c.c. *Con.* HNO₃ |
| NH₄Cl | 53.4 | Ammonium Chloride | 105 |
| K₄FeC₆N₆, 3H₂O | 456 | Potassium Ferrocyanide | 45.6 |
| KSCN | 97 | Potassium Sulphocyanate | 97 |
| BaCl₂, 2C₂O | 244 | Barium Chloride | 24.4 |
| Ba(NO₃)₂ | 261 | Barium Nitrate | 26.1 |
| CaSO₄, 2H₂O | 172 | Calcium Sulphate | Saturated: about |
| CaCl₂ | | | |
| MgSO₄, 7H₂O | | | |
| MgSO₄, 7H₂O NH₄Cl | | | |
| FeSO₄, 7H₂O | | | |
| FeCl₃, 6H₂O | | | |
| Fe₂(SO₄)₃, 9H₂ | | | |
| AgNO₃ | | | |
| HgCl₂ | | | |
| SnCl₂, 2H₂O | | | |
| PtCl₄, 8H₂O H₂PtCl₆ | | | |
| Co(NO₃)₂, 5H₂ | | | |
| KOH } KI { HgCl₂ } | | | |

*In preparing separately dissolv aid of heat. Wh ... to the ure, with constant stirring, until a *permanent* precipitate begins to form, then add the potassium hydrate, and make up to 1 litre. After standing for some time, the clear portion of the solution is to be drawn off for use.

...with constant stirring, until a
...drate, and make up to 1 litre.
...on is to be drawn off for use.

# INDEX.

113